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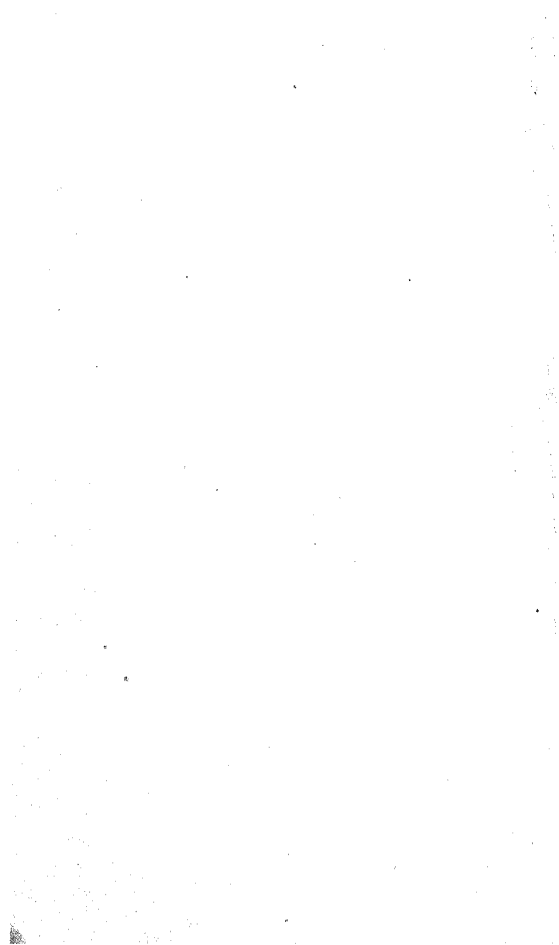




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 $C_{14}H_{14}N$   $\alpha$ -Indenyl-3-*n*-valeronitrile (INGOLD and THORPE), 154.  
 $C_{14}H_{16}N_2$  Diphenylethylenediamine, preparation of, and its sulphate (BENNETT), 576.  
 $C_{14}H_{16}O_5$  Anhydride of *cis*-lactonic acid,  $C_{14}H_{20}O_6$  (INGOLD and THORPE), 382.  
 Ethyl hydrogen 5-*cyclohexanespiro*dicyclopentan-3-one-1:4-dicarboxylate (INGOLD and THORPE), 361.  
 $C_{14}H_{20}O_6$  *cis*- and *trans*-Lactonic acids from  $\gamma$ -hydroxy- $\beta$ -*cyclohexyl*- $\alpha$ -ethyltricarballic acid, and their silver salts (INGOLD and THORPE), 380.  
 $C_{14}H_{20}O_7$  *cis*- and *trans*- $\gamma$ -Hydroxy- $\beta$ -*cyclohexyl*- $\alpha$ -ethyltricarballic acids, and their barium salts (INGOLD and THORPE), 381.

## 14 III

- $C_{14}H_8O_6N_{10}$  2:4:6:2':4':6'-Hexanitrodiphenylethylenedinitroamine (BENNETT), 577.  
 $C_{14}H_{10}ON_2$  Phenylphthalalazone, preparation of (MITTER and SEN), 1147.  
 $C_{14}H_{10}O_2N_2$  Phenylazophthalide (MITTER and SEN), 1147.  
 $C_{14}H_{10}O_{12}N_6$  Hexanitrodiphenylethylenediamine (BENNETT), 578.  
 $C_{14}H_{11}N_4As_2$  5:5'-Arseno-1:3:1':3'-benzodiazole, and its dihydrochloride (BAXTER and FARGHER), 1376.  
 $C_{14}H_{11}O_2N$  4:9-Dimethyl- $\psi$ -1:8-*ison*naphthoxazone, and its salts (DEY and GOSWAMI), 539.  
 $C_{14}H_{12}O_2N_2$  Phthalaldehydic acid phenylhydrazone (MITTER and SEN), 1146.  
 $C_{14}H_{16}O_2N$  Ethyl indenyl-2- and -3-cyanoacetates (INGOLD and THORPE), 150.  
 $C_{14}H_{16}ON_2$  Methylharmine, and its salts (PERKIN and ROBINSON), 947.  
 $C_{14}H_{14}O_3N_2$  Nitroso-5:6:7:8-tetrahydro-4:9-dimethyl- $\psi$ -1:8-*ison*naphthoxazone (DEX and GOSWAMI), 540.  
 $C_{14}H_{16}O_2N$  5:6:7:8-Tetrahydro-4:9-dimethyl- $\psi$ -1:8-*ison*naphthoxazone (DEY and GOSWAMI), 540.  
 $C_{14}H_{16}O_2N_2$  2-Acetyl-amino-5-*p*-acetylaminophenyl-4-methylglyoxaline, and its hydrochloride (FARGHER and PYMAN), 261.

$C_{12}H_{17}ON_3$  Benzyl isopropyl ketone semicarbazone (KON and THORPE), 703.

$C_{12}H_{17}O_2N_3$  Semicarbazone of 5-cyclohexanespirodiethylpentan-3-one-1-carboxylic acid (INGOLD and THORPE), 364.

$C_{12}H_{11}O_2N_3$  Semicarbazone of 5-cyclohexanespirocyclopentan-3-one-1-carboxylic acid (INGOLD and THORPE), 373.

12 IV

$C_{12}H_8O_4N_2Se_2$  Di-*m*-nitrophenyl diselenide (PYMAN), 170.

$C_{12}H_8O_2N_2As$  3:3'-Dinitro-4:4'-dihydroxydiphenylarsinic acid (FARGHER), 986.

$C_{12}H_{11}O_2N_2As$  3:3'-Dinitro-4:4'-diaminodiphenylarsinic acid (FARGHER), 989.

12 V

$C_{12}H_{11}O_2N_2ClAs$  3:3'-Diamino-4:4'-dihydroxydiphenylarsenious chloride, dihydrochloride of (FARGHER), 987.

$C_{13}$  Group.

$C_{13}H_{13}N$   $\alpha$ -Indenyl-3-*n*-butyronitrile (INGOLD and THORPE), 154.

$C_{13}H_{16}O_2$  *o*- and *p*-Hydroxybenzylidenemesityl oxide (GHOSH), 298.

$C_{13}H_{16}O_5$  *cis*-3-Hydroxy-4-cyclohexyl-1-methylcyclobutan-2-one-3:4-dicarboxylic anhydride (INGOLD and THORPE), 372.

*cis*-Lactonic anhydride from  $\gamma$ -hydroxy- $\beta$ -cyclohexyl- $\alpha$ -methyltricarballic acid (INGOLD and THORPE), 371.

$C_{13}H_{18}O_2$  5-cycloHexanespiro-2-ethylcyclopentan-3-one-1-carboxylic acid (INGOLD and THORPE), 379.

$C_{13}H_{18}O_4$  *cis*- and *trans*-3-Hydroxy-4-cyclohexyl-1-methylcyclobutan-2-one 3:4-dicarboxylic acids (INGOLD and THORPE), 371.

*cis*- and *trans*-Lactonic acids from  $\gamma$ -hydroxy- $\beta$ -cyclohexyl- $\alpha$ -methyltricarballic acid, and their silver salts (INGOLD and THORPE), 368.

$C_{13}H_{18}N_2$  2:5-Dimethyl-1-*n*-butylbenzimidazole, and its picrate (REILLY and HICKINBOTTOM), 178.

$C_{13}H_{20}O_4$  Acetyl derivative of 5-cyclohexanespirocyclopentan-3-ol-1-carboxylic acid (INGOLD and THORPE), 374.

$C_{13}H_{20}O_7$  *cis*- and *trans*- $\gamma$ -Hydroxy- $\beta$ -cyclohexyl- $\alpha$ -methyltricarballic acids, barium salts (INGOLD and THORPE), 369.

13 III

$C_{13}H_7O_4N$  6-Nitro-1:2- $\alpha$ -naphthapyrone (DEY and GOSWAMI), 540.

$C_{13}H_8O_2N_2$  Quinolinanil (GHOSH), 1103.

$C_{13}H_8O_2N$  9-Methyl  $\psi$ -1:8-*ison*naphthoxazone, and its salts (DEY and GOSWAMI), 539.

$C_{13}H_9O_2N_3$  Quinolinyphenylhydrazine (GHOSH), 1103.

$C_{13}H_{12}ON_2$  Harmine, and its salts (PERKIN and ROBINSON), 946.

Methylnorharmine (PERKIN and ROBINSON), 951.

$C_{13}H_{12}O_2N_2$  Nitroso-5:6:7:8-tetrahydro-9-methyl- $\psi$ -1:8-*ison*naphthoxazone (DEY and GOSWAMI), 539.

$C_{13}H_{13}ON$  Aceto- $\beta$ -naphthylmethylamide (MORGAN and EVANS), 1143.

$C_{13}H_{13}O_2N$  5:6:7:8-Tetrahydro-9-methyl- $\psi$ -1:8-*ison*naphthoxazone (DEY and GOSWAMI), 539.

$C_{13}H_{14}ON_3$  Harmaline, and its salts (PERKIN and ROBINSON), 951.

$C_{13}H_{13}N_2$  Keto-*ison*ormethyltetrahydroharmine (PERKIN and ROBINSON), 951.

$C_{13}H_{14}O_2N_4$  Acetyl-amino-4-*p*-acetylaminophenylglyoxaline, and its hydrochloride (FARGHER and PYMAN), 240.



## ERRATA.

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Page Line  
1198 6\* for "0·81617" read "0·81417."

# JOURNAL OF THE CHEMICAL SOCIETY.

## TRANSACTIONS.

### *The Conception of the Chemical Element as Enlarged by the Study of Radioactive Change.*

A Lecture delivered before the Chemical Society on  
December 19th, 1918.

By FREDERICK SODDY.

THE Council of the Chemical Society have honoured me with the invitation to deliver one of three lectures bearing on the ultimate constitution of matter, and I accepted the invitation in my desire to show how greatly I appreciated it rather than with any prospect of being enabled, when the time came, to say anything on the subject which has not already been said before. The problem of the ultimate constitution of matter belongs to another world than that through which for the past four years we have been living, and although hostilities have at length ceased, and we may look forward to an opportunity of resuming in the future the thread of our philosophical investigations, philosophy herself is not so easily to be resumed. Novel in one sense as are the ideas introduced into the concepts of physics and chemistry by the study of radioactivity, four years' interruption has made them appear rather as a remote historical accomplishment than as a contemporaneous development. Although no longer new, however, the more as the subject matures does it become apparent that these advances are of fundamental and increasing importance to the chemist.

One would perhaps have expected that on the first and most  
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fundamental conclusion arrived at in the study of radioactive change that the change is of a transmutational character, involving the spontaneous disintegration of the radio-element into others, it would have been the chemists who would have been most deeply interested, and who would have weighed the evidence and pronounced a decision. Yet judgment on the view, which was put forward more than fifteen years ago, on evidence in my opinion even then deserving of serious consideration, although accepted and universally adopted by the workers in the subject and by physicists, has gone by default so far as the majority of chemists are concerned. From the first, much of the most important evidence has been of a singularly simple and convincing chemical character.

*The Transmutational Character of Radioactive Change.*

If a chemist were to purify an element, say lead from silver, and found, on re-examining the lead at a later date, that silver was still present, and, again and again repeating the process, found always that silver, initially absent, reappeared, would he not be forced to conclude that lead was changing into silver and that silver was being produced by lead? It is because of the absence of evidence of this kind that the doctrine of the unchangeability of the elements has grown up. One positive example of the kind in question and that doctrine would be at an end. The conclusion to which in 1902 Sir Ernest Rutherford and I were forced with regard to the element thorium was based on evidence of this direct and simple nature. By simple purification, by chemical and physical means, constituents responsible for the greater part of the radioactivity of thorium can be separated, and as often as they are separated they are regenerated at a perfectly definite and regular rate. One of these constituents, the emanation, is gaseous, and it can be separated from the thorium by no more elaborate means than by a puff of air. Certainly the actual quantity of thorium emanation is infinitesimal, but this did not hinder its complete chemical characterisation, for it was found to pass unabsorbed through every reagent tried, one or other of which would have absorbed every known gas with the exception of the gases of the argon family. The conclusion that the thorium emanation was a gas of the argon family produced by thorium, later extended to the similar gaseous products of radium and actinium, was a purely experimental conclusion reached before any theory whatever as to the nature of radioactivity had been advanced.

Another constituent responsible for part of the radioactivity we

called thorium-X. It is left in the filtrate when a solution of thorium is precipitated with ammonia, although not when the thorium is precipitated by other reagents, such as sodium carbonate or phosphate. After this removal, however, thorium-X re-forms in the thorium. Moreover, it is thorium-X, not thorium, that produces the emanation. The latter in turn produces the non-volatile active deposit, in which the successive products, called thorium-A, -B, -C, and -D, are now recognised. The false interpretation of a similar phenomenon in the case of radium, before the radium emanation had been recognised, led to the view that inactive matter could be rendered temporarily radioactive by "induction," through contact with or association with radioactive matter. In the case of thorium, the discovery of the chemical character of the thorium emanation rendered the nature of the phenomenon clear almost from the first.

This, taken in conjunction with the atomic character of radioactivity, recognised by Mme. Curie from the start, and with the fact that the law of radioactive change proved to be the same as the law of unimolecular reaction, made the conclusion that the radio-elements were undergoing a series of successive changes, in which new elements are produced, of chemical and physical character totally distinct from those of the parent element, the only one capable of explaining the facts.

Novel and unexpected as it was to find transmutation spontaneously in progress among the radio-elements, the phenomena this explanation explained were equally novel and transcended what to a generation ago would have appeared to be the limits of the physically possible.

It is to pay chemistry a poor compliment to represent this conclusion as in any way contrary to the established foundations of chemistry. If it had not been for the correct conception of the nature of chemical change, the clear distinction between atoms and molecules, and the conclusion that in all changes in matter hitherto studied the element and the atom of the element remain essentially unchanged, which we owe to the founders of chemistry, the character of radioactivity would not have been arrived at so quickly. On the other hand, if radioactivity had not been almost instantly recognised as a case of spontaneous transmutation, then, if you will, there would have been something radically wrong with chemistry and the training it affords in the elucidation of the metamorphoses of matter.

With regard, however, to the various claims that have been made since that transmutational changes can be artificially effected, by the aid of the electric discharge in gases or the rays from radium,

I have always regarded the evidence in this field as capable of simple alternative explanation. Different investigators have obtained entirely opposite results, and there is not that consensus of evidence one finds among those who have investigated radioactive change.

In another direction there has been a tendency to underrate the unique and unparalleled phenomenon of radioactive change, and to connect what is entirely and solely a development of the new experimental science of radioactivity, with the somewhat older isolation of the electron and the electronic hypotheses of the constitution of matter to which that discovery have given rise. For example, Sir J. J. Thomson in his Romanes Lecture, 1914, says: "Since the electron can be got from all the chemical elements we may conclude that electrons are a constituent of all the atoms. We have thus made the first step towards a knowledge of the structure of the atom and towards the goal towards which since the time of Prout many chemists have been striving, the proof that the atoms of the chemical elements are all built up of simpler atoms—primordial atoms, as they have been called." The removal of electrons from matter occurs in physical, chemical, and radioactive changes alike, exemplified, respectively, by the electrification of a glass rod by friction, the ionisation of an electrolyte by solution, and by the  $\beta$ -ray change of radioactive substances. It is only in the latter case, however, that the electron can be regarded as a primordial constituent and the change as transmutational. Even to-day it is in radioactive phenomena, and in these alone, that the limits reached long ago in the chemical analysis of matter have been overstepped and the Rubicon, which a century ago Prout vaulted over so lightly in imagination, has actually been crossed by science.

#### *First and Second Phases of Development.*

Looking backward to the first recognition of the character of radioactive change in 1902, it is possible to distinguish broadly two phases. The first phase, concerned mainly with the disentanglement of the long and complicated series of successive changes, commencing with the two primary radio-elements uranium and thorium, and including ultimately all the known radio-elements, added little to the conceptions of chemistry beyond the disturbing fact that the radio-elements, although in every other respect analogous to the ordinary elements, are in process of continuous transmutation. But in the second and more recent phase of radioactive change, the study of the chemical character of the

successive products and the law connecting this with the type of ray expelled in the change, the discovery of elements with different radioactive but identical chemical character, the recognition of these as isotopes, or elements occupying the same place in the periodic table, and the interpretation of the significance of the periodic law, conceptions are arrived at which are not merely novel, but upsetting. In this phase, an aspect of the ultimate constitution of matter has been revealed that, although well within the scope of the conceptions of elements and atoms which we owe to the nineteenth century, nevertheless has totally escaped recognition. I am not much concerned with definitions, but I think the Chemical Society might safely offer a prize of a million pounds to any one of its members who will shortly and satisfactorily define the element and the atom for the benefit of and within the understanding of a first-year student of chemistry at the present time.

#### *Chief Features of Radioactive Change.*

The features that distinguish radioactive change from chemical change, and which have made it possible in a few short years to reduce to some degree of finality and completeness the intensely complicated series of successive changes suffered by the elements uranium and thorium in the course of their disintegration, are chiefly two. In the first place, the whole phenomena are inevitable, incapable of being changed or deviated from their allotted course by any means whatever, independent of temperature, concentration, or the accumulation of products of reaction, the presence of catalysts, irreversible and capable of being accurately and quantitatively followed without alteration or disturbance of the changing system. The mathematical theory, although for many successive changes it becomes cumbrous and unwieldy to a degree, involves only the solution of one differential equation by a device quite within the compass of anyone possessing a knowledge of the bare elements of the calculus to employ. The second feature is in the magnitude of the energy evolved, which, weight for weight of matter changing, surpasses that evolved in the most exothermic chemical changes known, from one hundred thousand to a million times. Manifested in the form of rays, by their fluorescent, photographic, or ionising power capable of being put into evidence in almost inconceivably minute amount, changes are capable of being followed, and by the electroscope accurately measured, which would conceivably require to continue for millions of years before they could be experimentally detected by chemical or even by spectroscopic methods. The disintegration of the single

atom is ascertainable, for example, in the spinthariscopes of Sir William Crookes, where each of the scintillations separately visible is due to the impact of a single  $\alpha$ -particle on the zinc sulphide screen. On the same principle, methods have been developed and are in regular use for counting the number of atoms disintegrating per minute, whereas to the spectroscope at least  $3 \cdot 10^{13}$  atoms as a minimum must be present, 25,000 times as many atoms as there are human beings alive in the world, before any element can be so detected. By the most curious compensation, almost of the nature of a providential dispensation which some may have found difficult to believe, the quantity of matter of itself is not of importance in investigating radioactive change. The methods depend on the rate of emission of energy, and this is proportional to the quantity of the changing element multiplied by its rate of change. In the disintegration series, the various members accumulate in quantities inversely proportional to the rates of change, and so it comes about that all changes within the series are equally within the scope of the method whether, as in the case of the parent elements, they involve periods surpassing the most liberal estimates of the duration of geological time or, as in the case of the  $C'$  members, are estimated to run their course in a time so short that light itself can travel but a very few millimetres, before the next change overtakes the changing atom.

The condition of radioactive equilibrium in which the quantities of the successive products assume the above stationary ratio is of course entirely different from chemical equilibrium, and is the condition in which for each member of the series except the first as much is produced as changes further in the unit of time.

The foregoing applies so long as the changes continue. When they are finished and it is a question of ascertaining the ultimate products, the task may be likened to that of searching for a meteor which a moment before lit up the heavens and now has vanished into the night.

#### *The Ultimate Products.*

It is a matter for surprise that in all radioactive changes so far studied there appear to be only two ultimate products, helium and lead, the former constituting the  $\alpha$ -particles and the latter being produced both by uranium and thorium, withal, as we now know, not the same lead in the two cases. There are sufficient experimental reasons for doubting whether the disintegration of an atom into more nearly equal parts would be within range of detection by any of the known methods. A heavy atom like oxygen, for example, if expelled as a radiant particle, might not attain

sufficient velocity to ionise gases, or, even if it did, the range over which the ionisation would extend, as we know from the ionisation produced by the recoil atoms, would be extremely small. It must be a matter for comment, however, that hydrogen never appears in these changes, as, if it were produced, it would almost certainly be as easy to ascertain as helium. It has always seemed to me a possibility that some genetic connexion may exist, after all, between thorium and uranium, although I have never been able to frame even a possible mode of so connecting these two elements. With a difference of atomic weight of six units, it is impossible to pass from one to the other by addition or expulsion of helium atoms alone.

Both with regard to helium and lead, the composition of radioactive minerals gave the first clue to the identity of the ultimate products. After the discovery of radioactivity and the elucidation of its nature, the fact that helium was found only in minerals containing uranium and thorium assumed a totally new interpretation, borne out by the spectroscopic proof of the production of helium from radium by Sir William Ramsay and myself, and later from actinium, polonium, and even from uranium and thorium, all at the rates to be expected from radioactive data. The identification of the  $\alpha$ -particle with helium, after the weight of the  $\alpha$ -particle had been shown by new physical methods to be four times that of the hydrogen atom, was accomplished by enclosing the radium emanation in a glass tube thin-walled enough to allow the  $\alpha$ -particle to go through, but perfectly impervious to the passage of gas. In these circumstances, helium in spectroscopically detectable quantity was proved by Rutherford to make its appearance outside the tube.

Such confirmations by the spectroscope, welcome and gratifying as they are, are nevertheless in a sense subsidiary to the main problem, namely, the task of unravelling the complicated series of changes into its individual steps, and the characterisation by their radioactivity of the several intermediate members of the series, such as by the determination of their periods and the physical constants of the radiation  $\alpha$ -,  $\beta$ -, or  $\gamma$ -, to which they give rise. The determination of their chemical character, although equally important, was only later fully accomplished.

### *The Radiations.*

In the successive radioactive changes,  $\alpha$ - or  $\beta$ -particles are expelled, one  $\alpha$ -particle per atom disintegrating for each change, although for the  $\beta$ -particles our knowledge is less exact. In some

cases, certainly, although these are exceptional,  $\beta$ -particles seem to be expelled along with  $\alpha$ -particles. The  $\alpha$ -particle is an atom of helium charged with two atomic charges of positive electricity, or, as we should now say, is the helium nucleus, deprived of the two electrons which are combined with it in the helium atom. The  $\beta$ -particle is the negative electron, and when expelled with sufficiently high velocity is accompanied with  $\gamma$ -rays. The latter are X-rays of exceedingly short wave-length, varying from 1.3 to 0.1 Ångström units.\* A connexion exists between the speed of the change and the speed of the particles expelled, and the more rapid the change the faster in general and the more penetrating are the attendant  $\alpha$ - or  $\beta$ -particles. In the case of the  $\alpha$ -particle, an empirical logarithmic relation, known as the Geiger-Nuttall relation, enables us to calculate approximately the period of the changing element from the velocity or range of the  $\alpha$ -particle, and vice versa, and by this means periods too long or too short to be directly measurable have been estimated. In the case of the  $\beta$ -rays, no definite quantitative law has yet been made out, but it is clear that a similar relationship must exist. One of the important corollaries is that changes much slower than the slowest known, namely, those of uranium and thorium, would probably not be detectable, as, even were  $\alpha$ - or  $\beta$ -particles expelled, they would be of too low velocity probably to ionise gases or show fluorescent or photographic actions. Indeed, for mesothorium-*I* and actinium this appears to be the case. No detectable radiation is expelled, although the products conform to what would occur in  $\beta$ -ray changes. The period of both substances is long, and it is probable that the  $\beta$ -particle is expelled, but is undetectable by ionisation methods. For the slowest  $\beta$ -ray change, that of radium-*D*, with a period of twenty-four years, the  $\beta$ -radiation is of such low velocity as to be only capable of detection by special care, and is far less penetrating than average  $\alpha$ -rays. These facts serve to show that changes may be going on in the non-radioactive elements which at present are beyond experimental means of detection.

#### *Period of Average Life.*

The law of radioactive change, which is the same for all cases, is that of unimolecular reaction, the rate of change, or quantity changing in unit of time, being a fraction, designated by  $\lambda$  and

\* The shortest wave-length so far resolved by the crystal reflection method is 0.072 Å. in the spectrum of the  $\gamma$ -rays of radium-*C*. Ishino and Rutherford have recently concluded, however, that the main  $\gamma$ -radiation of radium-*C* must have a wave-length lying between 0.02 and 0.007 Å. (*Phil. Mag.*, 1917. [vi], 33, 129; 34, 153.)



known as the radioactive constant, of the amount present. The value of  $\lambda$ , although vastly different for different radio-elements, is an absolute constant, so far as is known, for any one element, independent of every consideration whatever. The period of average life is the reciprocal of this constant, but the actual life of any one atom may assume any value. This is an experimental fact very difficult to account for. For example, it is quite easy to compare the value of  $\lambda$  for a collection of atoms (1) only just produced and not in existence a short interval before, and (2) that have remained undistinguished from an originally very much greater number, and each of which has been in existence many times the period of average life. In both cases the value of  $\lambda$  is the same. This fact excludes from consideration as a conceivable cause of disintegration any gradual progressive alteration in the atom during its period of existence, as, for example, was at one time suggested, a gradual radiation of internal energy by the electrons in their orbits within the atom. So far, we must admit, the cause of atomic disintegration remains unknown, although Lindemann (*Phil. Mag.*, 1915, [vi], 30, 560) has attempted, with some success, to frame a theory to account for it.

#### *Branch Series.*

The development of the various radioactive sequences revealed that sometimes the series branches, and that in the change of one radio-element sometimes two products result, in general, in different amounts. Thus the uranium series at one point branches into the radium and actinium series, in proportion 92 to 8 out of 100 atoms disintegrating. Again, in the case of radium-*C* and thorium-*C* a similar branching occurs, and here in one branch an  $\alpha$ -ray change is followed by a  $\beta$ -ray change, and in the other branch the sequence is reversed. These cases are sufficiently explained if it be supposed that two simple radioactive changes are in progress in the same substance simultaneously, and that each obeys the law of simple change as though the other did not occur. The distribution of the original substance into the two products is then proportional to the relative rates of the two changes. If  $\lambda_1$  and  $\lambda_2$  are the radioactive constants of the two changes, the proportion between the two products is as  $\lambda_1$  to  $\lambda_2$ , and the constant of the double change as a whole,  $\lambda_1 + \lambda_2$ . For thorium-*C*, the ratio is as 65 to 35, but for radium-*C* 99.97 to 0.03. The first is relatively easy, but the second extremely difficult to follow experimentally. It is, for example, impossible to follow further what occurs to the minor branch owing to the minuteness of the quantity

of material, and although this has to be represented as not further changing, we have only negative evidence to go on. This branching is very important as showing how from one element two products or more in very different quantity may result, and may be the explanation of the excessive rarity of certain of the elements in nature.

*History of the Analysis of Matter.*

The second, and in many respects even more revolutionary phase in the development of the study of radioactive change arose out of the chemical characterisation of the successive products, but some historical comment on the various influences which have gone to shape the current conception of the chemical element may be of interest before dealing with this development.

The analysis of matter into different chemical elements was at first concerned with known materials obtainable in abundance. The question, then, was not as to the existence or otherwise of certain elements, but whether certain thoroughly well-known substances were elements or compounds. Boyle's original celebrated definition was a purely practical one. That was to be regarded as elementary which could not by any means be separated into different substances. Almost at once, however, there crept into the interpretation of this conception two fallacies, or two aspects of the same fallacy, implicit in all the later characterisations of the elements, right up to the present time, namely, first that chemical analysis was necessarily the most fundamental and searching kind of material analysis, known or to be discovered, and, secondly, that chemical compounds were necessarily more difficult to resolve than simple mixtures. *Any* means soon came to mean any chemical means, and the element, in consequence, the chemical element. So was taken the first step which ultimately was to make the term *chemical element*, as it is at present understood, denote a definite but highly complex chemical conception, incapable of being defined or even understood without long years of training in the science, and totally different in every single respect from what a plain man or a beginner in the subject might reasonably suppose the term element ought to connote. The elementary and even the homogeneous character has departed from the conception of the chemical element, but the conception remains, and, whatever we choose to call it, will remain. The criterion of the chemical element soon came to be, in fact, the possession of a unique chemical character, distinguishing it and sufficing for its separation from all other elements. To this Dalton added a new criterion, the magnitude of the weight of the atom of the element, and each

element unique in chemical character (as it happened) proved also to possess a unique atomic weight.

The discovery of the periodic law introduced the idea of families of chemically analogous elements, the members of which recurred after regular intervals when the elements were arranged in order of atomic weight. With the exception of hydrogen, every element became one of a group all totally distinct, but with obvious similarities. Boyle's practical definition of the element as that which could not be further resolved, more and more, as the century advanced, fell into desuetude. It became replaced by a theoretical conception, to which subsequently I propose to apply the term "heterotope," meaning the occupant of a separate place in the periodic table of elements. With this place came to be associated the unique chemical character, unique atomic weight, and later unique spectrum. On the claims of a substance to the title of element, as in settling disputes as to what multiple of the equivalent was to be adopted as the atomic weight, the periodic law became the court of appeal. Did a claimant to the title of element fit into a vacant place in the family of related elements? If it did, not only was there no doubt as to its atomic weight, but it certainly could scarcely be an ordinary compound or mixture. Whatever the elements were, it was clear that they were all of a class, the limits of chemical analysis, and, if complex, then all probably of the same kind of complexity.

Incidentally, also, the periodic law showed that although there was a connexion between atomic weight and chemical character, there were exceptions, like tellurium and iodine, where the atomic weights appeared to have been reversed. This made it perfectly plain that it was merely a chance that no two elements happened to possess the same atomic weight. Dalton, as we shall come to describe, discovered in the atomic weight not merely a new atomic property, but a new class of atomic property which, until the present century, remained the only one of the kind known, and is concerned with a different region of the atom from that to which physical and chemical character, position in the periodic table, spectrum, and other identifying characteristics are to be referred.

The discovery of spectrum analysis led to the recognition of many new elements, caesium and rubidium, thallium, indium, helium, and gallium all being so recognised before anything at all was known as to their other properties. In each case unique spectrum was later found to correspond with unique chemical character—except for the argon gases, all characterised by absence of chemical character—and unique atomic weight.

Again, the first fruits of the discovery of radioactivity were the

recognition of the new elements polonium, radium, and actinium by their unique radioactive character in the first place. Then, in the case of radium, its claim to the title of element was confirmed, first by its exhibiting a unique spectrum, then by its possession of unique chemical character and atomic weight and by its occupying a vacant place in the periodic table. The emanations, next, as occupying a place in the family of argon gases, were easily characterised, and for the radium emanation unique spectrum was proved. Its origin from radium by loss of one  $\alpha$ -particle gives the atomic weight as 222, which agrees with determinations of its density and rate of diffusion. The chemical characters of polonium and of actinium are different from those of the elements they most closely resemble. Polonium, or radium-*F'*, by its close chemical analogy to both bismuth and tellurium, was characterised as an element of the sulphur family occupying the vacant place contiguous to bismuth. Actinium, by its resemblance in chemical character to the rare earths, and especially to lanthanum, although capable of being concentrated fractionally from that element, was reasonably supposed to occupy the vacant place in Group III, between radium and thorium. As will later appear evident, both these elements in due course may be expected to show unique spectra.

Further progress in the elucidation of the chemical character of successive products then underwent an abrupt and, at first, very puzzling change of direction. As member after member in the series was distinguished and characterised by its unique radioactive character, by its disintegration in definite and characteristic ways at definite and characteristic rates, no further *chemically* new elements were discovered. *Unique radioactive character does not always, as it did with radium, imply unique chemical and spectroscopic character.* The new members resembled known elements in chemical character so closely that they could not be separated from them by chemical analysis, although sharply differentiated from them by the radioactive properties. Radio-lead or radium-*D* cannot be separated from the lead which, being a product of uranium, accompanies it always in uranium minerals. Ionium, the direct parent of radium, cannot be separated from thorium; but the most instructive case, historically, which shows well how the new method of radioactive analysis serves to distinguish different elements, where chemical analysis fails, was the case of radiothorium.

*Chemically Non-separable Elements.*

Ramsay and Hahn, in the course of working up a large quantity of thorianite for radium, observed in fractionating the radium from the barium in the usual way that the activity of the material concentrated at both ends of the fractionation. The activity accumulating in the more soluble fractions was due to a new product, which they termed radiothorium. It produces thorium-X, the thorium emanation, etc., in successive changes. Naturally enough, they thought they had separated radiothorium by chemical processes from thorium, but they had not, for that, as we know, is quite impossible. Then Hahn found along with the other end fraction, containing the radium, a further new product, mesothorium, which is intermediate between thorium and radiothorium. The radiothorium they had separated from thorianite was not that present in the mineral when they started, but that which had re-formed from the mesothorium after it had been separated from the thorium in the mineral. Could any more elegant extension, not merely of knowledge, but of the means of obtaining knowledge, be imagined? Two different elements, thorium and radiothorium, which on account of their chemical resemblance could not be individually recognised, and in the original interpretation of the thorium disintegration series were taken as one, became individually knowable, because the latter is the product of the former through the intermediary of a third member, mesothorium, possessing chemical properties totally unlike either. Radioactive change thus became the means of a new analysis of matter, for which there is no counterpart outside the radio-elements.

In turn, mesothorium suffered analysis into two successive products, mesothorium-1 and -2, the first distinguished by long period of life and a rayless disintegration into the second, which has a short life and gives powerful  $\beta$ - and  $\gamma$ -radiation in its change into radiothorium.

I then found that mesothorium-1 was chemically non-separable from radium, a discovery also made by Marckwald at the same time, and in 1911 I pointed out that in an  $\alpha$ -ray change, such as ionium into radium, radium into emanation, thorium into mesothorium-1, and other cases, the expulsion of the  $\alpha$ -particle causes the radio-element to shift its place in the periodic table by two places in the direction of diminishing mass and diminishing valency, whereas in successive changes in which  $\alpha$ -particles are not expelled, it frequently reverts to its former position, as, for example, radiothorium from mesothorium and lead from radio-lead.

To those actually engaged in the task of trying to separate the

successive products of radioactive change by chemical analysis, it soon became clear that the chemical resemblances disclosed between certain of the members was such as to amount to chemical identity. The most obstinate cases of similarity previously known, among the rare earths, for example, cannot be compared with them. In all cases, radioactive methods afford the most delicate means for detecting the least alteration in the concentration of the constituents, and the most prolonged and careful attempts fail to produce a detectable separation.

At my request, Fleck undertook in my laboratory a systematic chemical examination of all the members of the series still imperfectly characterised, from the point of view of first finding which known element they most resembled and then finding whether or not they could be separated from that element. His researches were the means of finally unmasking the extreme simplicity and profound theoretical significance of the process of radioactive change. All the members of the series so far chemically uncharacterised he found to be chemically non-separable from one or other of the known elements, mesothorium-2 from actinium, radium-*A* from polonium, the three *B*-members and radium-*D* from lead, the three *C*-members and radium-*E* from bismuth, actinium-*D* and thorium-*D* from thallium.

#### *Radioactive Change and the Periodic Law.*

In February, 1913, K. Fajans in Germany, from electrochemical evidence, and in this country A. S. Russell and I independently, from Fleck's work, pointed out the complete generalisation which connects chemical character and radioactive change. In addition to the shift of two places in the periodic table caused by the expulsion of the  $\alpha$ -particle, it was now clear that the expulsion of the  $\beta$ -particle caused a shift of one place in the opposite direction. Since the  $\alpha$ -particle carries two atomic charges of positive electricity and the  $\beta$ -particle one atomic charge of negative electricity, the successive places in the periodic table must thus correspond with unit difference of charge in the atomic structure, a conclusion reached later for the whole periodic table, as far as aluminium, as the result of Moseley's investigations on the frequency of Barkla's characteristic X-radiations of the elements.

The non-separable elements, with identical chemical character, on this scheme were found all to occupy the same place in the periodic table, and on this account I named them isotopes. Conversely, the different elements recognised by chemical analysis should be termed "heterotopes," that is, substances occupying

separate places in the periodic table, but themselves mixtures, actually proved or potential, of different isotopes, not necessarily homogeneous as regards atomic weight and radioactive character, but homogeneous as regards chemical and spectroscopic character, and also physical character, so far as that is not directly dependent on atomic mass.

### *Spectra of Isotopes.*

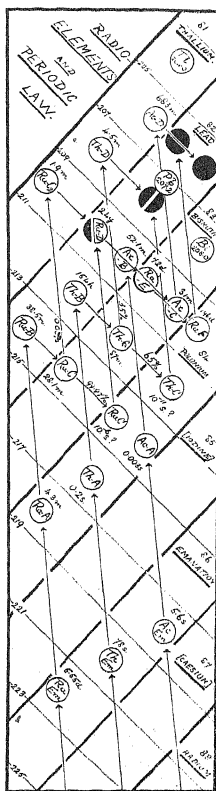
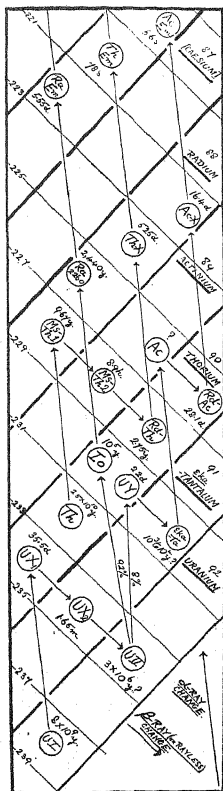
As regards the spectrum, the first indication that chemically non-separable elements probably possessed identical spectra arose out of the failure of Russell and Rossi and of Exner and Haschek in 1912 to detect any lines other than those of thorium in the spectrum of ionium-thorium preparations that might reasonably be supposed to contain an appreciable, if not considerable, percentage of ionium. The work of Hönigschmid on the atomic weight of ionium-thorium preparations has fully confirmed this view. The isotopes of lead of different atomic weight separated from uranium and thorium minerals have been found to possess identical spectra. For this element, lead, Rutherford and Andrade have shown that the secondary  $\gamma$ -radiation excited by the impact of  $\beta$ -rays on a block of ordinary lead gave by crystal reflection two lines identical in wave-length with the two strongest lines in the  $\gamma$ -ray spectrum of radium-B, an isotope of lead, as Fleck showed, of atomic weight 214. This is of importance as indicating that  $X$ -rays and  $\gamma$ -rays, although no doubt originating in a deeper region of the atom than the ordinary light spectrum, do not originate in the deepest region of all to which the weight of an atom and its radioactive properties are to be referred.

### *Description of the Figure.*

The generalisation, brought up to date, is set forth in the accompanying figure, which is to be read at an angle of  $45^\circ$ , making the lines of atomic weight horizontal and the division between the successive places in the periodic table vertical. Starting from uranium and thorium, the series run in an alternating course across the table and extend over the last twelve places as far as the element thallium. At this point, it is interesting to note that the expulsion of an  $\alpha$ - instead of a  $\beta$ -particle would have resulted in the production of an isotope of gold, and so literally have realised the goal of the alchemist. As it happens, a  $\beta$ -particle is expelled and lead results, so far as the changes have yet been traced, in all cases as the final product.

It has been necessary, in order to separate the series from one

another, to displace the actinium series to the right and the radium series to the left of the centre of the places, but this displacement



within the single place is not intended to express any physical significance; but for the fact that many members would be super-



imposed, they would all be represented in the centre of the places. The periods of average life, which are always 1.443 times the periods of half-change, are shown for each member above or below its symbol, a ? indicating that the period is estimated indirectly from the Geiger-Nuttall relation.

The figures at the head of each place represent the atomic numbers or number of the place in the periodic table, starting with hydrogen as unity, helium as 2, lithium as 3, and so on. Moseley found that the square-root of the frequency of the characteristic X-radiation of an element was, for the K-series of radiations, proportional to integers less by one than the atomic numbers. Strictly speaking, there is no means of determining the absolute value of the atomic number, but the starting point having been fixed for any one element, the others can then be found in terms of it. Moseley assumed the atomic number of aluminium as 13, as it is the thirteenth known element in the list starting with hydrogen as unity. It is unlikely that any new elements will be discovered between hydrogen and aluminium,\* although if they were it would be necessary to alter the whole of the subsequent atomic numbers to correspond. For X-radiations of the other series, the square-roots of the frequencies are not proportional to integers even, although the differences are nearly integral for successive elements in the periodic table. The actual numbers in the figure, 92 for uranium, for example, are derived from the assumption that the atomic number of aluminium is 13, but it is well to remember that, although relatively to one another based on experimental evidence, the absolute value is to some extent arbitrary.

#### *The Chemical Character of the Radio-elements.*

The simple connexion between the sequence of radioactive changes and the chemical character of the products has effected an enormous simplification, not only in the theory, but also in the practice of radio-chemistry. The series extends over twelve places, two, namely, those in the families of the halogens and the alkali metals, being entirely skipped. In the ten occupied places are forty-three distinct types of matter, but only ten *chemical* elements. Seven of these ten, thallium, lead, bismuth, emanation, radium, thorium, and uranium, can now in every respect be considered, both chemically and spectroscopically, thoroughly well

\* The position of the stellar elements of Prof. Nicholson it is unnecessary to consider here, as the Chemical Society is shortly to be given a first-hand account of this fascinating question.

known. These seven places accommodate all but nine of the known radio-elements, and these nine, the isotopes of polonium, actinium, and ekatantalum, respectively, are the only members the chemistry and physics of which cannot be referred to well-known elements obtainable in sufficient quantity for ordinary chemical and spectroscopic examination.

Of these three, polonium, although the element of which at present the chemistry is best known, is likely to remain the most difficult to bring into line with the others, for, although a vast amount of exact information has been obtained as to its reactions, it would seem to remain hopeless ever to obtain it in anything but infinitesimal amount owing to its relatively very short period.

The chemistry of actinium has been enormously simplified by the discovery that mesothorium-2 is isotopic with it, for the latter may be used as an indicator to show in what way the actinium distributes itself after any chemical treatment. Owing to its relatively small quantity as a branch product and to the fact that, itself, it gives no rays, the characteristic radioactivity of its products only making their appearance slowly after it has been separated, actinium has always been a difficult element to extract from the mineral and very easy to lose in chemical operations. There is now, however, another reason which will assist in the study of this element.

#### *The Origin of Actinium. Ekatanalium.*

The generalisation has now led to the elucidation of its origin and the discovery of its direct parent. From its constant association with uranium minerals, and the relative activity therein of its products in comparison with the activity of those of radium, it was considered to be a branch product of the uranium series, only 8 per cent. of the atoms of uranium disintegrating passing through the actinium series and 92 per cent. through the radium series. Its definite location in the periodic table, by virtue of its isotopy with mesothorium-2, made it clear that its parent must either be in the radium or the ekatanalium place, the former if it is produced in a  $\beta$ -ray change and the latter if it is produced in an  $\alpha$ -ray change.

The ekatanalium place was vacant when the generalisation was first made, but it was necessary to suppose that uranium- $X$ , like mesothorium, comprised two successive products, uranium- $X_1$  and uranium- $X_2$ , both giving  $\beta$ -rays, and the latter occupying the vacant place in question. This prediction was confirmed within a few weeks of its being made by the discovery by Fajans and

Göhring of uranium- $X_2$ , or brevium, a new member responsible for the more penetrating  $\beta$ -radiation given by uranium- $X$ , and having a period of only 1.65 minutes. The possibility that actinium was produced in a  $\beta$ -ray change from an isotope of radium was experimentally disproved, and there remained only the second alternative, which was rendered the more probable by the existence of a member, uranium- $Y$ , discovered by Antonoff, isotopic with uranium- $X_1$ , and simultaneously produced with it from uranium in relative quantity such as is to be expected, if it were the first member of the actinium series. Uranium- $Y$ , like uranium- $X_1$ , gives soft  $\beta$ -rays, and hence its unknown product must be the isotope of uranium- $X_2$ , and might also well prove to be the unknown direct parent of actinium in an  $\alpha$ -ray change of long period.

During the year the missing element has been found in two independent investigations (Soddy and Cranston, *Proc. Roy. Soc.*, 1918, [A], 94, 384; O. Hahn and L. Meitner, *Physikal. Zeitsch.*, 1918, 19, 208). The problem as it presented itself to us was so to treat a uranium mineral as to separate an element, if present, which possessed the chemical character of the known but hopelessly short-lived uranium- $X_2$ , using the latter as an indicator in trying possible methods beforehand. The method adopted, distillation at an incipient red heat in a current of carbon tetrachloride vapour and air, was found to be very effective in volatilising uranium- $X_2$  from uranium- $X_1$ , and when applied to pitchblende it was found to give a product in which none of the known pre-emanation members of the disintegration series were present. Thus was obtained a preparation from which actinium was at first absent, but which, with the lapse of time, continuously generated actinium, as characterised beyond the possibility of doubt by means of its active deposit.

It should be mentioned that the exact point at which the uranium series branches has not yet been definitely ascertained, as there is a choice of alternatives, at present experimentally indistinguishable. Uranium- $F$  may be either the product of uranium- $I$  or of uranium- $II$ , and the latter alternative, which is that shown in the figure, is taken for the present as likely to be on the whole the more probable. The point can only be settled by the determination of the atomic weight of ekatantalum or actinium.

Independently, Hahn and Meitner obtained the parent of actinium from the insoluble siliceous residues left after the treatment of pitchblende with nitric acid by adding tantalum, and then separating it and purifying it by chemical treatment. They showed that it gave  $\alpha$ -rays of range 3.314 cm. of air at *N.T.P.*, and, from this range, estimate its period to be from  $10^3$  to  $2 \cdot 10^4$

years. There should therefore be sufficient of the element in uranium minerals to enable the spectrum, atomic weight, and chemical character of the pure substance to be determined in the same way as for radium. Its separation on a large scale will enable actinium itself to be grown in a pure state, analogously to the preparation of radiothorium from mesothorium, and so should allow the spectrum at least of actinium to be found.

With regard to the period of actinium, there is at present a real conflict of evidence, and so it is impossible to say whether our knowledge of actinium is ever likely to become as complete as that of radium, or to remain, like that of polonium, confined to what can be learned from infinitesimal quantities. Cranston and I, on certain assumptions, concluded from indirect evidence that the period of actinium was 5000 years, but Hahn and Meitner, on the other hand, state that they have obtained evidence confirming Mme. Curie's provisional estimate of the period as about thirty years, from the direct observation of the decay of the radiations of a sealed actinium preparation.

#### *Atomic Weight of Isotopes.*

It is clear that the periodic law connects, not primarily chemical character and atomic weight, but chemical character and atomic charge or atomic number, which alters its value by integers, not continuously, producing the step-by-step changes in chemical character which is at the basis of the analysis of matter into the chemical elements, or heterotopes. This atomic number is, however, the algebraic sum of positive and negative charges, so that the loss of the  $\alpha$ -particle with its two positive charges and of two negative electrons as  $\beta$ -particles leaves its value unchanged and produces an isotope of the element having an atomic weight four units less than the original. Unique chemical character and unique spectrum reaction is no proof of homogeneity, and so we arrive at the conclusion that the chemical elements, so far considered homogeneous, may be mixtures of isotopes, possessing different atomic structure and stability, revealed when they undergo radioactive change, and in some cases also different atomic weight. This, although within the scope of the Daltonian analysis of matter to detect, nevertheless, until radioactive investigations revealed this possibility, remained overlooked. In two cases, that of the isotopes of lead on the one hand, and of ionium and thorium on the other, this difference of atomic weight in elements spectroscopically and chemically identical has now been established by direct determinations.

The figure shows that, so far as these changes have been followed, they all terminate in the place occupied by lead, and, if this is the real, as distinguished from the apparent end in all cases, all the ultimate products are isotopes of lead with atomic weight between 210 and 206. The product of radium- $C_2$ , in the branch claiming only 0.03 per cent. of the whole ultimate product of radium, with atomic weight 210, may be left out of account as being negligible, and also the product of the actinium branch for which the atomic weight is still uncertain; but the main products, namely, that of uranium with atomic weight 206, and both the thorium products in the two branches, with atomic weight 208, are different in different directions from that of common lead with atomic weight 207.2.

The conclusion that the ultimate product of thorium, as well as of uranium, was lead, was quite new and opposed to the opinion of those who had made a special study of the Pb/U and Pb/Th ratios of radioactive minerals of various geological periods. I found, however, that the atomic weight of the lead separated from Ceylon thorite was 207.7, and Hönigschmid confirmed this with a specimen of my material and obtained the figure 207.77. Just recently, from a specimen of lead separated from a Norwegian thorite by Fajans and his co-workers, he has found the value 207.90 (*Zeitsch. Elektrochem.*, 1918, **24**, 163). Whereas the same investigator, and also T. W. Richards and others, have found values for the atomic weight of lead separated from uranium minerals all lower than that of common lead, and in two cases from carefully selected minerals between 206.0 and 206.1. I found my thorite lead was denser than common lead in the same proportion as its atomic weight was greater, and the densities of the various specimens of uranium lead have been found by Richards to be less than that of common lead, the atomic volume for all varieties being constant. The spectra of these various isotopes have been repeatedly examined, but hitherto no differences whatever have been established.\*

The atomic weight of a mixture of ionium and thorium was found by Hönigschmid to be 231.51 as compared with 232.12 for thorium, the spectra being identical and impurities absent in both specimens. The calculated value for the atomic weight of ionium is 230, and the evidence, so far as it yet goes, is in accord with

\* Haskins and Aronberg (*Proc. Nat. Acad. Sci.*, 1917, **3**, 710), for ordinary lead and uranio-lead of atomic weight 208.34, examining the strongest line, 4058, in the sixth order of spectrum obtained by a 10-inch grating, observed a constant difference of 0.0043 Å., but are themselves disposed to await further results before drawing any conclusions.

the view that, in the mixture examined, about 30 per cent. was ionium and 70 per cent. thorium. By a simple comparison of the emanating power of the mixture with that of the pure thorium preparation under similar conditions, the proportion of ionium to thorium could be readily determined directly, since ionium does not give an emanation, and this unknown eliminated, but this has still to be done.

*The Different Varieties of Isotopes and Heterotopes.*

When isotopes, such as those just considered, possess different atomic weights, it is to be expected, although this has not yet been practically accomplished, that a separation by physical means, such as prolonged fractional diffusion, ought to be possible. Chlorine and other elements, the atomic weights of which depart largely from an integral value, seem to deserve a further physical analysis by this method. Sir J. J. Thomson's positive-ray method of gas analysis ought to be able to detect such isotopes of different atomic weight without separation, and at one time it seemed that neon had been so resolved, but this has not yet been confirmed.\* It would be interesting also if the rotation of the salts of some optically active acid with different varieties of lead, separated from uranium and from thorium minerals, were examined. A difference is to be expected, although it is likely to be small, and possibly may be too minute to be detectable. Recent experiments at Harvard have shown that the refractive index of a crystal of lead nitrate is independent of the atomic weight of the contained lead, but the solubility, as is to be expected, is different, the molar solubility of different varieties being the same.

Isotopes need not, however, have different atomic weights. One of the clearest cases is in the two end-products of thorium, but, if the scheme is correct as regards the branching point of the actinium series, ionium and uranium-*Y*, actinium-*A* and radium-*C'*, actinium-*C* and radium-*E*, actinium-*B* and radium-*D*, and the actinium and uranium isotopes of lead, are other cases. These result by branchings of the series, and, since in the respective branches the amount of energy evolved in the successive changes is different, the internal energy of the various pairs must be different, although for them atomic weight as well as spectroscopic and chemical character are all identical. I recently suggested in the case of the two end-products of thorium that possibly only one of these survives in geological time, namely, that produced in the

\* Mr. Ashton tells me this work is still being actively prosecuted at the Cavendish Laboratory.

smaller quantity, and that the other continues to break up in changes as yet undetected (Royal Institution Lecture, May 18th, 1917; *Nature*, 1917, **99**, 414 and 433). This would account for the relative poverty of thorium minerals in lead, which was the original basis for the conclusion that lead was not the ultimate product of thorium. The point still remains experimentally untested. Isobaric isotopes of the character in question can only at present be distinguished if they are unstable and break up further, but they must be taken into account in any theoretical conception we form of the ultimate structure of matter. The accomplishment of artificial transmutation would reveal them if they existed, and the discovery of any new property, like radioactivity, concerned with the nucleus of the atom rather than its external shell, might also be the means of revealing differences of this character.

On the other hand, the production of isobaric heterotopes is the ordinary consequence of  $\beta$ -ray changes, single or successive. Such heterotopes, possessing different chemical and spectroscopic character but the same atomic weight, have been recently termed *isobares* by A. W. Stewart (*Phil. Mag.*, 1918, [vi], **36**, 326), who, following Fleck's work on the chemical resemblance, not amounting to non-separability, between quadrivalent uranium and thorium, has drawn a parallel between them and elements existing in more than one state of valency, as, for example, ferrous and ferric iron.

The extent to which the study of radioactive change has enlarged the conception of the chemical element may be summarised by the statement that now we have to take into account in our analysis of matter, not only the heterobaric heterotopes before recognised, but also heterobaric and isobaric isotopes and isobaric heterotopes or isobares.

### *The Nuclear Atom.*

I have attempted to present the most important facts of radioactive change without introducing any theory or hypothesis at all as to the structure of the atom. I think it important to keep the two matters distinct. Our knowledge of electricity, which in its modern phase may be considered to start from the relatively recent discovery of the electron, is still far too imperfect to enable any complete theory of atomic structure to be formulated. My task would be incomplete, however, if I did not refer briefly to the nuclear atom of Sir Ernest Rutherford, which may be regarded as the logical descendant of the earlier electronic atom of Sir J. J. Thomson. The weakness of the latter was that it took account essentially only of the negative electrons, and its attempt to ascribe

the whole mass of the atom to these nearly massless particles involved the supposition that a single atom may contain hundreds of thousands of electrons. The actual number is now known to be rather less, as an average, than half the numerical value of the atomic weight. Although unsatisfactory in accounting for the mass of the atom on an electronic basis, it was much more in line with present views in accounting for chemical character and the arrangement of elements in the periodic table. The root idea that the successive elements in the table are distinguished by the increment of one electron in the outermost electronic ring, followed, as period succeeds period, by the completion of this ring and the formation of a new external one, so that members of the same chemical family have similar external ring systems, is still the most probable view yet advanced. In conjunction with the conception of the nucleus and the gradual unravelling of the various series of characteristic X-radiations, both experimentally and by mathematical analysis, it bids fair soon to give a definite concrete picture of the structure of all the different elements (compare L. Vegard, *Phil. Mag.*, 1918, [vi], 35, 293).

As regards the deepest region of atomic structure, wherein radioactive phenomena originate, the nuclear atom is the only one proposed that has any direct experimental foundation. It is based on the deflections suffered by the  $\alpha$ -particle in its passage through the atoms of matter, on the one hand, as Bragg showed many years ago, on the exceedingly slight deviation of the overwhelming majority of the  $\alpha$ -particles, and, on the other, on the subsequently discovered large deviations suffered by a minute proportion. The nuclear atom is a miniature solar system, like most model atoms, the negative electrons occupying the atomic volume by their orbits around a relatively excessively minute central sun or nucleus, wherein the atomic mass is concentrated, and consisting of an integral number of atomic positive charges equal to the atomic number of the element, and the number of electrons in the outer shell. An  $\alpha$ -particle is the nucleus of the helium atom, and, unless it passes very near the nucleus of the atom through which it penetrates, its path is practically undeflected. The few that chance to pass close to the exceedingly small but massive central nucleus are swung out of their path like a comet at perihelion, save that the forces at work are regarded as repulsive rather than attractive.

It appears from radioactive change that atomic disintegration occurs always in the central nucleus, both  $\alpha$ - and  $\beta$ -particles originating therein. The atomic number of the element is its nett nuclear charge, the difference between the positive and



negative charges entering into its constitution. Of all properties, mass and radioactivity alone depend on the nucleus; the physical and chemical character and the spectrum of an element originate in the outer shell. The character of the outer shell is fixed by the nett charge, not at all by the mass or internal constitution of the nucleus, and the integral variation of this charge from 1 to 92 gives the successive places of the periodic table. Expulsion of two  $\beta$ - and one  $\alpha$ -particle in any order gives an isotope of the original element with atomic weight four units less. Isobaric isotopes resulting in branch changes differ only in the internal structure and stability of the nucleus. The atomic mass is the only nuclear property known before the discovery of radioactivity, and, except as regards this, the whole of physics and chemistry up to the close of the nineteenth century had not penetrated beyond the outer electronic shell of the atom. Even now, mass and radioactivity remain the sole nuclear properties known.

#### *Conclusion.*

Nemesis, swift and complete, has indeed overtaken the most conservative conception in the most conservative of sciences. The first phase robbed the chemical element of its time-honoured title to be considered the ultimate unchanging constituent of matter; but since its changes were spontaneous and beyond the power of science to imitate or influence to the slightest degree, the original conception of Boyle, the practical definition of the element as the limit to which the analysis of matter had been pushed, was left essentially almost unchanged.

The century that began with Dalton and ended with the discoveries of Becquerel and the Curies took the existing practical conception of the chemical element and theorised it almost out of recognition. The element was first atomised, and then the atom was made the central conception of the theory of the ultimate constitution of matter, on which modern chemistry has been reared, and from which its marvellous achievements, both practical and theoretical, have mainly sprung. The atom and the element became synonyms, related as the singular to the plural, and implicit throughout this century was the assumption that all the atoms of any one element are identical with one another in every respect. The only exception is in Sir William Crookes's conception of "meta-elements" as applied to the rare earths. Here the idea was rather that of a gradual and continuous difference among the different atoms of the same element, the properties of the latter

being the mean of those of its individual atoms. Modern developments have tended definitely away from rather than towards this view.

The second phase in the development of radioactive change has now negatived each and every one of the conceptions of last century that associated the chemical element with the atom. The atoms of the same chemical element are only chemically alike. Unique chemical and spectroscopic character is the criterion, not of a single kind of atom, but rather of a single type of external atomic shell. Different chemical elements may have the same atomic mass, the same chemical element may have different atomic masses, and, most upsetting of all, the atoms of the same element may be of the same mass and yet be an unresolvable mixture of fundamentally distinct things. Present-day identity may conceal differences for the future of paramount importance when transmutation is practically realised. Then it may be found that the same element, homogeneous in every other respect, may change in definite proportion into two elements as different as lead and gold. The goal that inspires the search for the homogeneous constituents of matter is now known to be, like infinity, approachable rather than attainable. The word homogeneity can in future only be applied, qualified by reference to the experimental methods available for testing it.

All this, of course, does not in the least affect or minimise the practical importance of the conception of the chemical elements as understood before these discoveries. Every chemist knows the conception has had and will continue to have a real significance as representing the limit of the spectroscopic and chemical analysis of matter which remains, although it now is known to convey something very different from the original and natural conception of the chemical elements as the *l m n*'s of the material alphabet.

I.—*The Dilution Limits of Inflammability of Gaseous Mixtures. Part III. The Lower Limits of some Mixed Inflammable Gases with Air. Part IV. The Upper Limits of some Gases, Singly and Mixed, in Air.*

By HUBERT FRANK COWARD, CHARLES WILLIAM CARPENTER, and  
WILLIAM PAYMAN.

PART III.

IN Part I of this series of papers (Coward and Brinsley, T., 1914, 105, 1859), the wide variation in the values assigned by different observers to the limits of inflammability of hydrogen and other gases in air was shown to be due to the very different criteria of inflammability used. The meaning of the term "inflammability" was therefore discussed, and it was concluded that inflammability could and should be regarded as a characteristic property of a gas mixture, apart from the precise means used for ignition and from the form of the vessel that might happen to be chosen for experiment. It was argued that a gaseous mixture should be termed inflammable *per se* at a stated temperature and pressure if, and only if, it were capable of indefinite self-propagation of flame, while the unburnt portion of the mixture was maintained at the stated temperature and pressure.\*

In Part II (T., 1914, 105, 1865), the lower limits of inflammability of hydrogen, methane, and carbon monoxide individually in air were examined experimentally by means of apparatus specially designed to enable the progress of flame to be observed in much wider and longer vessels than had been hitherto employed.†

The present paper records the results of experiments carried out to determine the lower limits in air of various mixtures of hydrogen, methane, and carbon monoxide taken two at a time or

\* This definition has been discussed by Burgess and Wheeler (T., 1914, 105, 2591). Several other papers on the subject of "dilution limits of inflammability" have appeared since Coward and Brinsley's paper was published, but as they have not been concerned with the question of indefinite propagation of flame, but merely with the inflammation of very limited amounts of gaseous mixtures, they have no direct bearing on the present inquiry.

† Burgess and Oberfell (U.S.A. Bureau of Mines, *Technical Paper*, No. 119, 1915) have adopted a eudiometer of the same size as that used by Coward and Brinsley.

all three together, and, finally, of the complex mixture, a "town's gas."

A simple formula, of purely additive character, has been put forward by Le Chatelier to connect the lower limits of single gases with the lower limits of mixtures of them. This formula, originally limited to binary mixtures, is generalised thus:

$$\frac{n_1}{N_1} + \frac{n_2}{N_2} + \frac{n_3}{N_3} + \dots = 1.$$

where  $N_1, N_2, N_3 \dots$  are the lower limits, in percentages of the whole air mixture, for each combustible gas separately,  $n_1, n_2, n_3 \dots$  are the proportions, in percentages of the whole air mixture, of each combustible gas at the dilution limit. The percentage of total combustible gas present in the limit mixture is thus  $L = n_1 + n_2 + n_3 + \dots$

This formula enables the lower limit,  $L$ , of a combustible mixture to be calculated from the dilution limits of its several constituents. If the proportions of each of the combustible constituents are  $p_1, p_2, p_3 \dots$ , so that  $p_1 + p_2 + p_3 + \dots = 100$ , a simple transformation gives its dilution limit in air as

$$L = n_1 + n_2 + n_3 + \dots = \frac{p_1}{N_1} + \frac{p_2}{N_2} + \frac{p_3}{N_3} + \dots$$

The physical meaning of the formula may be best appreciated by the consideration of a particular case. A mixture of air, carbon monoxide, and hydrogen which contains one-quarter of the amount of carbon monoxide necessary to form a lower limit mixture, together with three-quarters of the amount of hydrogen necessary, will be a lower limit mixture. In other words, the lower limits of inflammability form a series of inflammability equivalents for the individual gases of a mixture.

It may also be deduced from the formula that lower limit air mixtures, if mixed in any proportions, give rise to mixtures which are also at their lower limits.

Experimental support for the formula rests on observations by Le Chatelier (*Ann. des Mines*, 1891, [viii], 19, 388) with three mixtures of methane and coal gas, by Le Chatelier and Boudouard (*Compt. rend.*, 1898, 126, 1344) with three mixtures of hydrogen and carbon monoxide and with one mixture of acetylene and carbon monoxide, and by Eitner (*Habilitationsschrift*, München, 1902) with hydrogen and carbon monoxide in equal volumes and with coal gas. The difference between the calculated and the observed dilution limits rarely reached one twenty-fifth part of

the combustible mixture. None of these experiments, however, was carried out in apparatus large enough to indicate whether the mixtures used were capable of continued propagation of flame. Thus, Le Chatelier and Boudouard used for the lower limit of hydrogen in air the figure 10 per cent., whereas the recent experiments have shown that mixtures containing upwards of 4.1 per cent. of hydrogen are capable of propagating flame apparently indefinitely in an upward direction. Le Chatelier had, in fact, found that the 10 per cent. hydrogen mixture was the weakest which would propagate flame downwards through a somewhat narrow tube. It is only necessary to ignite from below to produce a self-propagating flame in mixtures considerably weaker in hydrogen.

The experiments now to be described were therefore carried out in the eudiometer previously described (Coward and Brinsley, *loc. cit.*), 1.8 metres (6 feet) in length and 30 cm. (1 foot) square in section, with a capacity of 170 litres.

In each case, the mixtures under experiment were saturated with moisture at 18—19°, and were maintained at approximately atmospheric pressure during inflammation. The source of ignition was a spark gap of variable length between small platinum spheres. A 6-inch Apps coil with two, four, or six storage cells was used to produce single sparks. The various gases were prepared in a state of purity, and each mixture with air was made to the desired composition, which was checked by the analysis of samples taken just before firing.

#### EXPERIMENTAL.

The lower limits of a number of mixtures of hydrogen, carbon monoxide, and methane, taken two or three together, and also of a "town's gas," are recorded in table I (p. 30), together with the lower limits calculated by means of the Le Chatelier formula from the limits of the individual gases.

Several of the experimental results differ from those calculated by amounts exceeding the errors of observation and experiment; nevertheless, the formula gives a useful approximation over the whole range of mixtures examined, and may be applied, therefore, to water gas and to coal gas, as well as to town's gas.

The most striking anomaly was shown by the mixture containing 10 per cent. of hydrogen and 90 per cent. of carbon monoxide, where the large difference was in the opposite direction to that usually noted. This anomaly was more pronounced in experiments with the same mixture in a narrower tube (5 cm. diameter).

TABLE I.

Composition of gas (before admixture with air).			Lower limit of inflammability in air.		
Hydrogen.	Carbon monoxide.	Methane.	Observed. Per cent.	Calculated. Per cent.	Difference. Per cent.
100	—	—	4.1	—	—
75	25	—	4.7	4.9	-0.2
50	50	—	6.05	6.2	-0.15
25	75	—	8.2	8.3	-0.1
10	90	—	10.8	10.4	+0.4
—	100	—	12.5	—	—
—	90	10	11.0	11.1	-0.1
—	75	25	9.5	9.6	-0.1
—	50	50	7.7	7.7	0.0
—	40	60	7.2	7.1	+0.1
—	25	75	6.4	6.5	-0.1
—	—	100	5.6*	—	—
25	—	75	4.7	5.0	-0.3
50	—	50	4.6	4.7	-0.1
75	—	25	4.1	4.4	-0.3
90	—	10	4.1	4.2	-0.1
100	—	—	4.1	—	—
33.3	33.3	33.3	5.7	6.0	-0.3
55	15	30	4.7	5.0	-0.3
"Town's gas" †			5.35	5.36‡	0.0

\* This figure is chosen, rather than the lower value given by Coward and Brinsley (*loc. cit.*, p. 1885) for the reason stated on page 1877 of that paper: ". . . the flames of mixtures containing 5.3 to 5.6 per cent. of methane are very sensitive to extinction by shock . . . a 5.6 per cent. mixture will invariably propagate flame when the shocks are no greater than those occasioned by the somewhat violent bubbling of gas through water . . . (but) when the circumstances are such that a tranquil passage is assured, 5.3 per cent. is the lower limit of inflammability of methane in air." In none of the present experiments with methane mixtures did we observe the curious tranquil passage of flame noted with the 5.3 per cent. methane mixture, so that 5.6 per cent. seems the correct figure to employ for calculations in connexion with these experiments.

† Composition of the "town's gas":  $C_2H_6$ , etc., vapours = 0.8.  $CO_2$  = 2.6.  $O_2$  = 0.5.  $C_2H_4$  etc. = 2.8.  $CO$  = 14.1.  $H_2$  = 46.6.  $CH_4$  = 19.4.  $C_2H_2$  = 4.0.  $N_2$  = 9.2 per cent. The benzene, etc., vapours were estimated by the determination of their partial pressures, by Burrell and Robertson's method (*J. Ind. Eng. Chem.*, 1915, 7, 669).

‡ For calculating this figure, the following lower limits of the individual gases were used: Hydrogen, carbon monoxide, and methane, as in table I, ethylene 3.4 per cent. (Eitner), ethane 3.1 per cent. (Burgess and Wheeler), benzene 1.4 per cent. (Kubierschky). The last three values represent results obtained in small vessels, but may probably be safely used in view of the comparatively small amounts of the three gases present in the "town's gas."

The non-inflammable constituents of the town's gas amounted to 12.3

A brief reference to the general character of the flames is necessary. Inflammable mixtures rich in hydrogen, including the town's gas, gave thin vortex rings of flame, increasing in diameter as they rose through the first 30 or 40 cm., and then breaking into luminous segments, which subdivided into balls of flame. The latter rose, increasing in number, to the top of the vessel. The flames in mixtures somewhat below the lower limit were extinguished at some stage of their journey. The flames of these mixtures showed, in fact, similar behaviour to those described by Coward and Brinsley for pure hydrogen, but the luminosity was much enhanced. Inflammable mixtures containing no hydrogen gave thick rings which, as they progressed, developed into flames of strongly convex front spreading from side to side of the box; similar mixtures just below the limit of inflammability gave rings of flame breaking into striæ, which were extinguished in the next 50 or 100 cm. of their journey. The appearance of all the flames of mixtures is apparently compounded additively of those of the individual components.

There was no difficulty in deciding upon the figure for the limit within about 0.1 per cent.

### *Conclusions (Part III.).*

The lower limits of inflammability, in air, of mixtures of hydrogen, carbon monoxide, and methane, taken two at a time or all together, and also the lower limits of water gas, coal gas, and town's gas, may be calculated with approximate accuracy from the lower limits of the individual gases by means of Le Chatelier's formula.

### PART IV.

#### *The Upper Limits of some Gases, Singly and Mixed, in Air.*

The upper limits of inflammability of hydrogen, methane, and carbon monoxide severally in air have been investigated by a number of observers; their results are quoted in T., 1914, 105, 1859. The hydrogen figures show the greatest range of variation, namely, from about 55 to 80 per cent. of hydrogen. The methane figures mostly lie between 12 and 17 per cent. of methane, and per cent., which on the lower limit mixture represents only 0.66 per cent. of the whole. In view of the known slight influence on the lower limit of methane of the substitution of small amounts of carbon dioxide or nitrogen for equal amounts of air, it is safe to assume for the purposes of the calculation that the non-inflammable constituents of coal gas (and likewise of water gas) can be treated as air.

the carbon monoxide figures are in the neighbourhood of 75 per cent. of carbon monoxide.

*The Upper Limit of Hydrogen.*—Some preliminary experiments were conducted with the object of discovering whether the flames in mixtures just below the upper limit resembled the flames in mixtures just above the lower limit. If so, the apparent discrepancies between the results of earlier workers might be explained on the same lines as the discrepancies noted in lower limit figures. It was soon evident, however, that comparatively weak or short electric sparks, which were quite strong enough to ignite lower limit mixtures, were unable to inflame upper limit mixtures. Stronger sparks in the latter mixtures started flames which travelled throughout the whole mixture. This promised a clue to the main cause of discrepancy of the results of others, and by the use of igniting sparks of such variable strength as might well have been employed in ordinary laboratory practice, a range of results was obtained nearly as wide as those of the previous uncorrelated list. The experiments were carried out in a half-litre globe with a spark of variable length in the centre. A 6-inch Apps induction coil was used with a constant break, and the current in the primary was varied by using a battery of 2 to 12 volts. We have to acknowledge our indebtedness to Mr. F. Brinsley for conducting this series of experiments, the results of which are recorded in table II.

TABLE II.

*Percentage of Hydrogen in Apparent Upper Limit Air Mixture.*

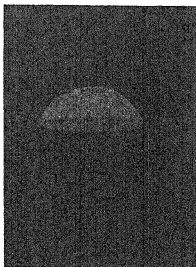
Spark gap.	Voltage of accumulators.			
	2	4	8	12
1 mm.	57.5	—	67.0	—
2	—	—	70.2	—
4	—	—	71.2	—
8	70.2	70.7	71.2	72.2
16	—	—	72.5	—
20	—	—	—	74.5
32	—	—	73.5	—
45	—	—	—	75.5
56	—	—	73.5	—

These figures suggest an upper limit of hydrogen-air mixtures in the neighbourhood of 75.5 per cent. of hydrogen, but the volume of gas used was much too small to indicate whether the flames observed were capable of indefinite self-propagation. Furthermore, the gases were confined, and so were not maintained under constant pressure during inflammation.





FIG. 1.



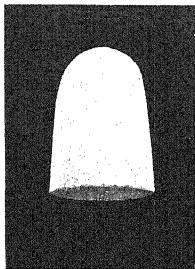
*Hydrogen.*

FIG. 2.



*Methane.*

FIG. 3.



*Carbon monoxide.*

FIG. 4



*Methane and carbon monoxide  
mixture.*

*Upper limit flames, in tube of 5 cm. diameter.*

A series of experiments was therefore carried out in a 15-litre bell-jar, just dipping under the surface of water, with a spark gap near the bottom of the mixture. With a suitable single spark, ignition was obtained with mixtures containing 73.1, 73.8, and 74.0 per cent. of hydrogen, but failed with 74.4 and 75.0 per cent. of hydrogen. The flames travelled rapidly throughout the whole mixture. The limit indicated was thus approximately 74.2 per cent. of hydrogen.

The next step in determining the true limit for continued propagation of flame was the use of long vessels. A tube 1.5 metres long and 5 cm. wide was used. Flame travelled rapidly through this tube with mixtures containing 71.2 and 71.4 per cent. of hydrogen. The appearance of this flame is indicated in Fig. 1. Mixtures containing 71.6 and 73.0 per cent. could not be ignited, or, if ignited, the flame was extinguished before it had travelled more than a few cm. from the spark.

In order to fix the upper limit precisely, it would be necessary to use vessels of dimensions comparable with those of the box previously described. This would involve the construction of a much stronger vessel than the one available, but at the time this was contemplated, the experiments had to be abandoned, and opportunities for continuing them will not be available in the near future.

It is, however, certain that the upper limit of hydrogen is somewhat higher than 71.5 per cent.; it is probably near to 74.2 per cent.

*The Upper Limit of Methane.*—In the 15-litre bell-jar, mixtures containing 15.1 and 15.3 per cent. of methane propagated flame, of a reddish-brown colour edged with blue, upwards throughout the mixture. A 15.5 per cent. mixture could not be ignited, but when a rapid succession of sparks was passed, a blue flame-cap was observed above them.

In the 1.5-metre tube, mixtures containing 14.4, 14.7, 15.0, and 15.1 per cent. of methane propagated flame throughout the tube; with a 15.2 per cent. mixture, a flame was initiated, but was extinguished after passing some cm. up the tube. In each case, the flame seemed to consist of two distinct portions, the uppermost blue with a convex front, followed by a reddish-brown conical tail, which suggested a secondary reaction of combustion (see Fig. 2). The limit for indefinite propagation is therefore more than 15.1 per cent., and probably approaches 15.4.

This conclusion is supported by the experiments of Burrell and Oberfell (*loc. cit.*), who used for upper limit experiments on methane an iron pipe 30 cm. (12 inches) in diameter, 2.1 metres

(7 feet) high, with a series of glass windows. Their experiments showed the upper limit to lie between 15.0 and 15.4 per cent. for upward propagation of flame.

*The Upper Limit of Carbon Monoxide.*—In the 15-litre bell-jar, flames travelling rapidly upwards through the whole of the mixture were obtained when 73.7 and 74.0 per cent. of carbon monoxide was present. Flames were initiated in 74.5 and 75.0 per cent. mixtures, but were extinguished after travelling a short distance. A 75.2 per cent. mixture gave only a blue halo round the spark.

In the 1.5-metre tube, a flame travelled up through a 72.9 per cent. mixture, but no more than a tongue of flame was obtained with a 73.1 per cent. mixture. The walls of the tube evidently exerted a notable cooling influence. The self-propagating flame had a strong convex front, was blue with a bright whitish-blue edging, but had no "tail," as was the case with methane flames (see Fig. 3).

The limit for indefinite propagation is therefore more than 73.0 per cent., and probably approaches 74.2 per cent.

#### *Applicability of the Mixture Law to Upper Limits of Inflammability.*

The additive character of the lower limits of inflammability was expressed by Le Chatelier in a formula quoted above (p. 28). The validity of a similar formula for the upper limits of mixed combustible gases in air has been obscured by experiments with hydrogen-air mixtures in which the sparks were insufficiently strong, and therefore the figures obtained represented, not the limiting composition for the propagation of flame, but the limiting composition for the initiation of flame by the sparks in use. It is shown below that the following formula holds approximately for the upper limits of mixtures of hydrogen, methane, and carbon monoxide, two or three at a time:

$$\frac{n_1}{N_1} + \frac{n_2}{N_2} + \dots = 1$$

where  $n_1, n_2, \dots$  represent the proportions, in percentages of the whole air mixture, of each combustible gas, at the upper limit,  $N_1, N_2, \dots$  represent the upper limits, in percentages of the whole air mixture, of each combustible gas separately.

For reasons stated above, the experimental apparatus available did not combine the desirable width with the desirable length, and the choice lay between a bell-jar and a longer but narrower

glass tube (1.5 metres long, 5 cm. in diameter). The latter was chosen because it enabled a flame to be observed travelling far enough from the original source of ignition; the disadvantage of narrowness was not great, for the limits observed in the tube were lower than those indicated by the wider bell-jar by a not very considerable amount. (For hydrogen, 2.7 on 74.2 per cent.; for methane, 0.25 on 15.4 per cent.; for carbon monoxide, 1.2 on 74.2 per cent.)

The limits observed in the tube are recorded in table III.

TABLE III.

	Percentage composition of gas (before admixture with air)			Upper limit of inflammability, in air.		
	H <sub>2</sub> .	CH <sub>4</sub> .	CO.	Observed.	Calculated.	Difference.
Single gases ...	100	—	—	71.5	—	—
	—	100	—	15.1	—	—
	—	—	100	73.0	—	—
Binary mixtures.	48.5	51.5	—	22.6	24.4	-1.8
	50	—	50	71.8	72.5	-0.7
	—	50	50	22.8	25.0	-2.2
Ternary mixture .....	33.3	33.3	33.3	29.9	31.9	-2.0
Coal gas .....	See footnote.*			30.9	28.8†	+2.1

\* Composition of the coal gas. C<sub>6</sub>H<sub>6</sub>, etc.=1.2; CO<sub>2</sub>=0.1; O<sub>2</sub>=0.1; C<sub>2</sub>H<sub>4</sub>=2.9; CO=7.3; H<sub>2</sub>=50.6; CH<sub>4</sub>=29.7; C<sub>2</sub>H<sub>6</sub>=3.2; N<sub>2</sub>=4.9 per cent.

† For the calculations, the upper limits of hydrogen, methane, and carbon monoxide given in the table were used, together with the values C<sub>6</sub>H<sub>6</sub>=4.7 (Roszkowski); C<sub>2</sub>H<sub>4</sub>=22.0; C<sub>2</sub>H<sub>6</sub>=10.7 (Burgess and Wheeler, ignition centrally in large globe. Private communication).

Analyses of the residual gases showed that mixtures just below the upper limit propagated flames which consumed the whole of the oxygen, and therefore passed through the whole of the mixture. This behaviour is in sharp contrast with that of lower limit mixtures, in which self-propagating flames may leave unconsumed a considerable fraction of the mixture.

Figs. 1, 2, and 3 show that the upper limit methane flames are characterised, in contradistinction from the hydrogen and carbon monoxide flames, by the possession of flame tails. Mixtures containing methane with carbon monoxide or hydrogen and air also exhibit the remarkable tail, which suggests a secondary reaction (see Fig. 4). Evidence as to the nature of this reaction should be readily obtained by an examination of the interconal gases,

but the opportunity of attempting this experiment has not presented itself.

*Conclusions (Part IV.).*

The upper limits of inflammability in air, saturated with water at 18—19°, of hydrogen, methane, and carbon monoxide are in the neighbourhood of 74·2, 15·4, and 74·2 per cent. respectively.

The upper limits in air of mixtures of these gases, taken two or three at a time, and also the upper limit of coal gas, may be calculated with approximate accuracy by means of a simple formula of an additive character.

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## II.—*The Propagation of Flame through Tubes of Small Diameter. Part II.*

By WILLIAM PAYMAN and RICHARD VERNON WHEELER.

IT is a common practice at collieries to test the safety of the miners' flame lamps, before they are taken underground, by introducing them into an inflammable mixture of coal-gas and air.

It is known that the speed of propagation of flame in mixtures of coal-gas and air can be considerably faster than in any mixture of methane and air. Since any inflammable mixture into which a miner's lamp may accidentally be introduced in the practice of coal mining is produced exclusively by fire-damp, and since it is a rare occurrence for fire-damp to contain even traces of any inflammable gas other than methane, the use of mixtures of coal-gas and air for testing the security of a lamp for use underground is justifiable only on the grounds of providing an adequate "margin of safety." The use of coal-gas becomes unjustifiable if the margin of safety thereby provided is excessive; for every additional protective device embodied in the construction of a miner's flame safety-lamp militates against the proper ventilation of the lamp, and therefore diminishes its light-giving power.

It is thus of importance to be able to make an exact comparison between the speeds of propagation of flame in mixtures of coal-gas and air and fire-damp, or methane, and air under similar conditions of experiment. Furthermore, since the rapid speed of flame in coal-gas-air mixtures is, presumably, due mainly to the hydrogen contained therein, and since different qualities of coal-gas contain

different proportions of hydrogen, it is necessary to obtain information regarding the effect of varying the proportions of the constituent gases in coal-gas on the speed of propagation of flame in its mixtures with air.

Following the same methods of experiment as with mixtures of fire-damp and air (T., 1918, 113, 656), the speeds of the uniform movement of flame in mixtures with air of coal-gas, hydrogen, and a 1:1 methane-hydrogen mixture have been determined in glass tubes of different small diameters for comparison with the results obtained with fire-damp-air mixtures in similar tubes. Comparative experiments have also been made on the projection of flame through brass tubes of small diameter.

For the experiments with mixtures of coal-gas and air, a supply of gas from the main was stored over alkaline water in a metal gas-holder of 70 litres capacity; and the mixtures with air were made in smaller glass gas-holders from this supply. In this manner, variations in the composition of the coal-gas, such as would have occurred had the gas for each mixture been drawn direct from the main, were avoided.

Rather more gas was required to complete the series of experiments than was anticipated, so that it was found necessary to re-charge the storage-holder before all the information desired was obtained.

From one point of view this was unfortunate, for the second charge of gas differed slightly in composition from the first, and mixtures with air of the one could not be directly compared with mixtures with air of the other. From another point of view, however, the enforced use of samples of coal-gas of different compositions was not to be regretted, for there were found to be marked differences in the speeds of propagation of flame in mixtures with air of the two qualities of gas. This observation led at once to the determination of the speeds of flame in mixtures with air of what may be termed a "synthetic coal-gas," containing equal parts by volume of methane and hydrogen. The results obtained, taken in conjunction with the known values for methane-air and hydrogen-air mixtures under the same conditions of experiment, are of considerable theoretical interest, whilst they should also prove of practical value.

According to Le Chatelier ("Le Carbone," p. 266. Paris, 1908), if several combustible gases are mixed together with air, the following relation exists at the lower limit of inflammability of the mixture, between the limits of inflammability  $N$  and  $N'$  of each of two gases and their proportions  $n$  and  $n'$  in the limit mixture:

$$n/N + n'/N' = 1.$$

Coward, Carpenter, and Payman have shown (this vol., p. 28) that this formula can be applied with considerable accuracy to a number of mixtures of gases, and that it holds also at the upper limit of inflammability.

The formula implies that if a limit mixture with air of one inflammable gas is mixed in any proportion with a limit mixture with air of another inflammable gas, a limit mixture results. Another way of stating the relation, in an expanded form, is as follows:

$$L = 100 \left( \frac{a}{L_a} + \frac{b}{L_b} + \dots \right) \dots \quad (i)$$

By means of this equation, the limiting percentage,  $L$ , for a mixture of gases can be found directly from the known limits of the individuals;  $a, b, \dots$  being the percentages of the individuals in the mixed inflammable gases, and  $L_a, L_b, \dots$  their respective limits.

The subject of the calculation of the limits of inflammability of mixed combustible gases is introduced here because a similar formula holds with remarkable accuracy (considering the nature of the phenomena under investigation) for calculating the speeds of flame in mixtures with air of a composite combustible gas like coal-gas, the speeds in mixtures of the individual gases with air being known. The formula is:

$$S = \frac{a+b+\dots}{a/S_a+b/S_b+\dots} \dots \quad (ii)$$

in which  $S$  is the speed required;  $a, b, \dots$  the percentages of the different combustible gases in the mixed gas (coal-gas, for example); and  $S_a, S_b, \dots$  the corresponding speeds of flames in mixtures of the individuals with air.

This formula necessarily finds its readiest application in the calculation of the speeds in distinctive mixtures, namely: (1) the limit mixtures, upper and lower, in which the speed of flame is slowest; and (2) the mixtures in which the speeds of flame are fastest. For such mixtures, the agreement between calculated and observed speeds is close.

In the table that follows are given: (1) the limits of inflammability, with horizontal propagation of flame in a glass tube 9 mm. in diameter, for hydrogen, methane, and a mixture of equal parts of hydrogen and methane; and (2) the speeds of the uniform movement of flame, in a horizontal glass tube 9 mm. in diameter, with the lower- and upper-limit mixtures and in the mixtures with the fastest speeds of flame, for hydrogen, methane, and the 1:1 hydrogen-methane mixture. The calculated limits and speeds for



the hydrogen-methane mixture, as determined by equations (i) and (ii), respectively, are also given.

			Speeds of uniform movement of flame. Cm. per second.		
			Mixture with fastest speed.		
	Limits.	Per cent.	Lower-limit mixture.	Upper-limit mixture.	
	Lower.	Upper.			
Hydrogen .....	6.7	65.7	8.3	430	(50)
Methane .....	7.8	11.6	32.6	49	35.6
Hydrogen- methane mixture } (Obs.)	7.2	19.6	13.7	96	17.1
} (Calc.)	7.2	19.7	13.2	90	(42)

The value obtained for the speed of propagation of flame in the upper-limit mixture of hydrogen and air is not the true value, which should approximate to that of the speed in the lower-limit mixture. The probable reason for the discrepancy is explained later. Omitting this value, and the calculated value for the speed of flame in the upper-limit mixture of hydrogen-methane-air based on it, it will be seen that there is a close correspondence between the calculated and the observed values for the limits and speeds.

With coal-gas, the gases that preponderate are hydrogen and methane, which in the two samples, *A* and *B*, used for these experiments totalled 83.5 and 85 per cent. respectively. Ignoring the other gases, calculation according to equation (ii) gives 106 and 96 cm. per second, respectively, as the maximum speed obtainable during the uniform movement of flame in a tube 9 mm. in diameter in mixtures of each sample of coal-gas with air. The speeds as determined by chronographic means were 106.2 and 94 cm. per second.

The proportion of mixed gases to be added to air to give mixtures with the fastest speed of the uniform movement of flame can also be calculated, knowing the corresponding values for each individual gas. The fastest speed with mixtures of methane and air is obtained over the range 9.5—10.0 per cent. of methane; with mixtures of hydrogen and air, the range is 38—45 per cent. of hydrogen. Using the same type of formula as for calculating the limit mixtures, the "fastest speed mixtures" of air with mixed combustible gases are found to be as follows:

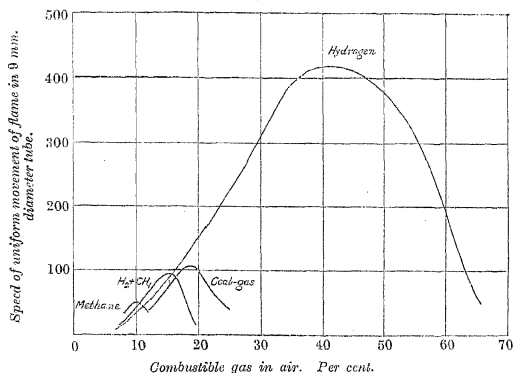
Mixtures with air in which the speed of the uniform movement of flame is fastest.		
Combustible gases.	Per cent. of combustible gas.	
Hydrogen-methane,	Calculated.	Observed.
(1 : 1) .....	15.2—16.3	15.0—16.0
Coal-gas A .....	17.5—18.8	18.0—19.0
Coal-gas B .....	16.3—17.5	16.5—17.5

If equation (ii) is expressed in the form

$$a/S_a + b/S_b + \dots = \frac{a+b+\dots}{S_{a+b+\dots}}$$

it is at once apparent that the inverse of the speed of flame in mixtures of a composite gas with air is a simple additive property of the inverse of the speed of flame in each constituent gas with air. In other words, the time taken for flame to spread through a given volume of a mixture of combustible gases with air, under the conditions of combustion during the uniform movement, is the mean of the times taken for flame to spread through the same

FIG. 1.



volume of mixtures of each constituent gas with air if present alone.

No doubt this relation, which has been shown to hold true for the fastest and the slowest speeds of the uniform movement of flame, is true also, as suggested by the generalisation just stated, for intermediate speeds. So that, given the necessary data respecting the individual combustible gases, the behaviour of flame in any mixture of several with air can be deduced. The exposition of the validity or otherwise of this assumption, when three or more combustible gases in varying proportions are used, will form the subject of a subsequent communication.

In Fig. 1 are shown, plotted to the same scale, the speed-per-

centage curves, for the uniform movement of flame in a horizontal glass tube 9 mm. in diameter, for hydrogen and methane, for a 1:1 mixture of hydrogen and methane, and for coal-gas (sample A).

The curve for hydrogen is constructed from Haward and Otagawa's determinations (T., 1916, 109, 85), with additional figures obtained near and at the limiting percentages. In this connexion, it should be noted that Haward and Otagawa, though they made no attempt to determine accurately the limits of inflammability for horizontal propagation of flame, considered that in a tube 9 mm. in diameter flame would not travel horizontally in mixtures containing less than 11.8 or more than 63.5 per cent. of hydrogen. Actually, the limits under the conditions thus specified are 6.7 (lower) and 65.7 (upper) per cent. It was found that when igniting mixtures near the limits of inflammability, great care had to be exercised to avoid disturbance at the mouth of the tube, and for that reason a lighted taper, such as was employed by Haward and Otagawa, which answered admirably over the range of mixtures studied by them, was unsuitable.\*

\* The details of the determinations made to locate the limits of inflammability of hydrogen-air mixtures in a horizontal tube 9 mm. in diameter are as follow: the tube was 1.5 metres long and the mixtures were ignited by a secondary discharge across a 5 mm. gap 4 cm. from the open end of the tube.

Lower limit. Hydrogen, per cent.	Result.
9.4	Flame travelled throughout.
7.5	" " "
7.1	" " "
6.8	" " "
6.6	Incomplete propagation of flame.

These results place the lower limit at 6.7 per cent. hydrogen. A mixture of this composition when tested failed three times to propagate flame, but on five occasions flame travelled throughout the length of the tube. The flames travelled very slowly and were only visible when the room was in complete darkness.

Upper limit. Hydrogen, per cent.	Result.
63.5	Rapidly moving flame throughout.
64.5	" " "
65.0	" " "
65.3	" " "

With mixtures containing 66 per cent. or more of hydrogen a sharp report occurred on sparking, due to the rapid combustion of a mixture made poorer in hydrogen by diffusion between the point of ignition and the open end of the tube. Flame also travelled rapidly over short distances towards the closed end of the tube; thus, with 67.5 per cent. hydrogen the flame travelled 25 cm., and with 67.8 per cent. 10 cm. With 68 per cent. no flame could be

Attention should be directed to the slow speed, 8.3 cm. per second, at which flame could travel in a mixture of hydrogen and air at the lower limit, a fact which illustrates the well-known persistence of hydrogen flames. In conformity with the results obtained for other gases, it was expected that the flame in the higher-limit mixture would be equally slow. The fact that so high a speed as 50 cm. per second was recorded was due to the difficulty experienced in igniting the mixture before diffusion at the mouth of the tube could decrease the percentage of hydrogen there.

The coal-gas was made at the carbonising plant of the Experimental Station, and was not diluted with water-gas. The analyses of the two samples were:

	Sample A. Per cent.	Sample B. Per cent.
Benzene and higher olefines .....	1.2	1.6
Carbon dioxide .....	0.1	nil
Ethylene .....	2.9	2.8
Carbon monoxide .....	7.3	7.1
Hydrogen .....	50.6	47.0
Methane and higher paraffins .....	32.9	38.0
Nitrogen (by difference) .....	5.0	3.5

It will be seen that the difference between the two samples of gas lay almost entirely in the proportions of hydrogen and paraffins that they contained; and from a comparison between the speed-percentage curves for coal-gas *A* and the hydrogen-methane mixture given in Fig. 1, it is evident that the slower speed of flame obtained with coal-gas *B* as compared with coal-gas *A* is due to the higher methane-content of the former. For the highest speed obtainable with the hydrogen-methane mixture, which contained 50 per cent. of each constituent, is considerably slower than the highest speed obtainable with coal-gas *A*, which also contained 50 per cent. of hydrogen, but only 33 per cent. of methane.

The results obtained on the propagation of flame in horizontal glass tubes of smaller internal diameter than 9 mm. are recorded in the tables that follow. The determinations were made in the same manner, and the numbers in the table have the same significance, as in the experiments with methane and air (*loc. cit.*, p. 658), with which they should be compared.

observed to travel away from the open end of the tube. These results place the upper limit for self-propagation of flame between 65.3 and 66.0 per cent. hydrogen. The determination was completed as follows:

Hydrogen, per cent.	Result.
65.9	Flame travelled rapidly about 40 cm.
65.7	
65.6	Complete "propagation" of flame. "

TABLE I.

*Coal-gas, Sample A.*

Internal diameter of tube, mm.	Coal-gas in mixture. Per cent.								
	12.4	13.1	16.4	17.5	18.4	19.2	20.0	22.7	24.5
2.0	nil	nil	nil	nil	nil	nil	nil	nil	nil
3.0	(25)	(50)	—	—	81.3	—	—	nil*	—
4.2	(25)	49.6	—	—	87.3	—	—	nil*	—
5.0	(30)	53.5	—	—	98.1	—	—	35.3	—
6.0	(44)	55.5	—	—	99.1	—	—	40.6	nil*
7.1	(52)	58.7	86.8	97.7	103.7	102.7	90.3	50.6	nil*
8.0	(60)	59.2	87.4	98.8	104.2	103.9	91.8	57.0	29.8

TABLE II.

*Coal-gas, Sample B.*

Internal diameter of tube, mm.	Coal-gas in mixture. Per cent.				
	13.1	14.0	14.8	16.5	16.8
2.0	nil	nil	nil	nil	nil
3.0	nil	—	60	—	—
4.2	(35)	—	—	—	—
5.0	(35)	—	—	—	—
6.0	(41)	—	—	—	—
7.1	(52)	62.2	71.4	84.1	80.1
8.0	(57)	63.2	77.4	85.8	82.3

TABLE III.

*Hydrogen-Methane, 1:1.*

Internal diameter of tube, mm.	Hydrogen-methane in mixture. Per cent.										
	8.45	9.45	11.90	13.90	14.35	14.95	15.95	17.20	18.10	18.65	19.55
2.0	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil
3.0	—	—	56.3	74.9	—	74.5	73.0	nil*	—	—	—
4.2	—	nil	57.9	75.9	—	—	—	46.1	nil*	—	—
5.0	—	(28)	59.4	83.1	—	86.0	84.0	53.5	nil*	—	—
7.1	(30)	38.7	63.0	85.1	88.0	95.8	94.1	74.1	43.3	nil*	—
8.0	(40)	39.4	69.5	87.1	90.7	—	—	75.8	49.4	34.2	nil*

\* Flame travelled towards the open ends of the tubes, a distance of 3 cm.

The results recorded in table III are shown as smoothed curves in Fig. 2, which illustrates the extent to which the "limits" are dependent on the environment of the inflammable mixture. It will be seen that the range of mixtures over which continued (horizontal) propagation of flame was possible became gradually restricted as the diameter of the tube was decreased, until with a

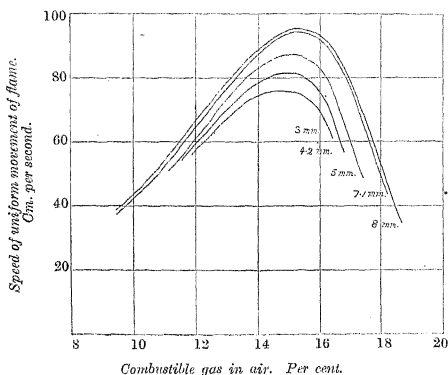
## 44 PROPAGATION OF FLAME THROUGH TUBES OF SMALL DIAMETER.

3 mm. tube it was less than half of that obtaining in a 9 mm. tube.

With a tube 2 mm. in diameter, no flame could travel away from the point of ignition, whatever the percentage of combustible gas present, an observation that applies also to the mixtures of coal-gas and air. With all mixtures of methane and air, a diameter of 3.6 mm. prevented the propagation of flame; whereas with hydrogen and air (30 per cent. hydrogen), Mallard and Le Chatelier (*Ann. des Mines*, 1883, [viii], 4, 320) have recorded the propagation of flame in a glass tube only 0.9 mm. in diameter.

Complementary to these results are the results of experiments

FIG. 2.



made on the passage of flame in mixtures of coal-gas and air through brass tubes, either open at both ends or arranged as extensions to a larger vessel, at the closed end of which the mixture was ignited. It is unnecessary to give the details of these experiments, which were conducted in the same manner and exhibited the same general features as the experiments with methane. It is sufficient to record that the flame in an 18 per cent. mixture of coal-gas *B* and air passed through 15–18 cm. length of brass tube of 4.4 mm. internal diameter placed horizontally and open at both ends, and was projected from a closed vessel (20 cm. long) through 13–15 cm. length of the same brass tubing. The corre-

sponding distances when a 10 per cent. mixture of methane and air was used were 7·5 and 3—4 cm. respectively.

The general conclusion to be drawn from these experiments as regards the testing of miners' safety-lamps is that "coal-gas" is an unsuitable gas to employ for that purpose, for the following reasons:

(1) Comparatively small variations in the composition of coal-gas affect the speed at which flame can travel in its mixtures with air. In particular, a reduction in the proportion of paraffins which it contains, such as is usually accompanied by an increase in the proportion of hydrogen when, as generally, carburetted water-gas is employed to dilute the coal-gas, enables a much higher speed of flame to be attained than can be given by mixtures of methane and air.

(2) Even with gas produced solely by the carbonisation of coal at normal retort temperatures, the speed of propagation of flame attainable is more than double that possible in mixtures of methane and air.

(3) It would seem that the ability of flame to pass through tubes or holes of small diameter is not dependent alone on its speed, although this is the main factor, but is to a certain extent a quality of the inflammable gas concerned. Flame in mixtures of hydrogen and air possesses the property of being able to pass through holes of very small diameter, and the presence of hydrogen in coal-gas confers this property in a certain degree on the flame in mixtures of the latter with air.

ESKMEALS,  
CUMBERLAND.

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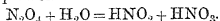
### III.—*Mixtures of Nitrogen Peroxide and Nitric Acid.*

By WILLIAM ROBERT BOUSFIELD, K.C.

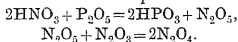
NITRIC acid and nitrogen peroxide are mutually soluble in certain proportions, and in other proportions give rise to a double layer. When to the simple binary mixture water is added, a more complex mixture arises. A systematic study of these mixtures was projected, beginning with the simple binary mixture and passing on to consider the modifications which are introduced by the addition of water. The present communication deals with the first

part only of this research. The nitric acid and nitrogen peroxide for the research have been specially prepared by Nobel's Explosives Co., Ltd., with whose chief research chemist, Mr. Rintoul, I have been in consultation from time to time.

*Nitrogen Peroxide.*—Nitrogen peroxide absorbs moisture readily, and in the absence of excess of nitric acid appears to decompose according to the equation

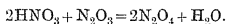


The presence of a very small quantity of water will therefore change the colour of liquid nitrogen peroxide to a dirty green, but traces of moisture may involve the presence of nitrogen trioxide without noticeable change of colour. Two samples of liquid nitrogen peroxide were supplied by Messrs. Nobel. Nearly all the work was done with sample No. 1, which was subsequently found to have contained traces of nitrogen trioxide. Sample No. 2 had been purified by distilling it with phosphoric oxide. The probable reactions which result in this purification appear to be

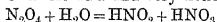


This sample, No. 2, may be regarded as pure liquid nitrogen peroxide.

In the meantime, before receiving this pure sample, I had used up sample No. 1 in nitric acid solutions and recovered it by distillation and rectification with a pear still-head. This sample, to which I may refer as No. 3, appears by the density given below to be nearly as pure as No. 2. This is probably due to the oxidation of the nitrogen trioxide by nitric acid, according to the equation



Thus with excess of nitric acid and very little water the reaction



appears to be reversed, and in the presence of excess of nitric acid the water appears to have no decomposing effect on the nitrogen peroxide.

As further evidence of this, the addition of a few drops of water to the orange-coloured liquid nitrogen peroxide turns it a dirty dark green, presumably due to the mixture of the blue nitrogen trioxide or nitrous acid with the orange nitrogen peroxide, but the addition of a few drops of nitric acid destroys the green and restores the orange colour.

The green colour cannot be eliminated by simple rectification, as the nitrogen trioxide and peroxide appear to pass off together, the resulting gas being of a somewhat deeper red colour than that of pure nitrogen peroxide. Nor does the addition of syrupy phos-



phoric acid help matters. Solid phosphoric oxide appears to be necessary to get rid of the nitrogen trioxide unless excess of nitric acid is added.

Another sample (No. 4), of a bulk of about half a litre, which had been accidentally contaminated with sufficient water to turn it to the dark green colour, was mixed with sufficient nitric acid to restore the orange colour and then distilled with phosphoric oxide. The resulting sample, No. 5, was of the same colour and density as the pure sample, No. 2. In the rectification of sample No. 4, the first few c.c. passed over green at a temperature at the top of the still-head of 19–20°. The bulk, which constitutes sample No. 5, distilled at  $21.9 \pm 0.1^\circ$ , which may be taken as the boiling point of pure liquid nitrogen peroxide.

TABLE I.

*Specific Volumes of Samples of Nitrogen Peroxide.*

	4°.	11°.	18°.
No. 1 .....	0.67390	0.68110	0.68864
No. 2 .....	0.67435	0.68172	0.68938
No. 3 .....	0.67432	0.68168	0.68935
No. 4 .....	—	—	0.68946
No. 5 .....	—	0.68170	—

A set of density observations on sample No. 1 was taken at the temperatures given in table II, which gives the observed specific volumes and those calculated from the formula

$$v = 0.66994 + 0.0009767t + 0.00000344t^2.$$

TABLE II.

*Specific Volumes of Sample No. 1 at Various Temperatures.*

<i>t.</i>	<i>D.</i>	<i>v</i> observed.	<i>v</i> calculated.	Difference.
0.08°	1.49250	0.67002	0.67002	±
7	1.47704	0.66703	0.67695	—8
11	1.46822	0.68110	0.68110	±
15	1.45909	0.68536	0.68536	±
18	1.45214	0.68864	0.68863	—1
20	1.44750	0.69085	0.69085	±

For the pure sample No. 2 the specific volume-temperature curve derived from the three duplicated observations at 4°, 11°, and 18° is

$$v = 0.67027 + 0.0010075t + 0.000003t^2,$$

which may be taken as giving the correct specific volume of pure nitrogen peroxide at temperatures from 0° to 20° within  $\pm 2$  in the fifth place of decimals

*Nitric Acid.*—The nitric acid used was specially purified and sent to me by Messrs. Nobel with the following analysis:

Nitric acid .....	99.68	per cent.
Hydrochloric acid .....	0.007	" "
Sulphuric acid .....	0.068	" "
Nitrous acid.....	0.012	" "
Mineral matter .....	nil	
	99.767	" "

I have taken the percentage of water by difference as 0.233 per cent.

The densities of this acid at the temperatures indicated are:

4°.	11°.	18°.
1.5381	1.5254	1.5126

In calculating the strength of the various mixtures of nitric acid and nitrogen peroxide, to which reference is made later, the nitrous acid given in the above analysis has been reckoned as nitrogen peroxide, since, for the reasons above given, it is assumed that with very concentrated nitric acid the nitrous acid present is oxidised to give nitrogen peroxide and water.

In table III are given the resulting values of the specific volumes, derived from the density determinations.\*  $P$  is the percentage by weight of nitrogen peroxide in the mixture. The temperature coefficients,  $\alpha$ , from 4° to 11° and from 11° to 18°

TABLE III.

*Specific Volumes of Mixtures of Nitric Acid and Nitrogen Peroxide.*

$P$ .	$v_4$ .	$v_{11}$ .	$v_{18}$ .	Temperature-coefficients.	
				4—11° $\alpha \times 10^5$ .	11—18° $\alpha \times 10^5$ .
0	0.65015	0.65557	0.66113	77	79
1.2168	0.64839	0.65374	0.65920	76	78
8.021	0.63719	0.64211	0.64715	70	72
16.88	0.62372	0.62821	0.63291	64	67
26.09	0.61214	0.61655	0.62113	63	65
34.925	0.60445	0.60885	0.61346	63	66
37.60	0.60296	0.60743	0.61204	64	66
42.01	0.60112	0.60568	0.61044	65	68
43.71	0.60082	0.60543	0.61026	66	69
46.70	0.60088	0.60561	0.61059	68	71
48.66	0.60113	0.60599	0.61110	69	73
49.96	0.60145	0.60639	0.61161	71	75
51.37	0.60205	0.60715	0.61248	73	76
53.10	0.60341	0.60873	0.61436	76	80
93.86	—	—	0.68610	—	—
96.93	0.67305	0.68030	0.68786	104	108
98.49	0.67371	0.68098	0.68855	104	108
100.00	0.67435	0.68172	0.68938	105	109

\* The actual density determinations have been omitted at the request of the Publication Committee to save space.

TABLE IV.

*Contraction of Mixtures of Nitric Acid and Nitrogen Peroxide.*

P.	Contraction per c.c. of solution.			Contraction per gram of solution.		
	4°.	11°.	18°.	4°.	11°.	18°.
1.22	0.0032	0.0033	0.0034	0.0021	0.0022	0.0023
8.02	0.0234	0.0242	0.0251	0.0149	0.0156	0.0163
16.88	0.0489	0.0506	0.0521	0.0305	0.0318	0.0330
26.09	0.0724	0.0743	0.0763	0.0443	0.0458	0.0474
34.92	0.0896	0.0917	0.0938	0.0542	0.0559	0.0575
37.60	0.0934	0.0954	0.0976	0.0563	0.0580	0.0597
42.01	0.0985	0.1005	0.1025	0.0592	0.0609	0.0626
43.71	0.0997	0.1017	0.1036	0.0599	0.0616	0.0632
46.70	0.1008	0.1027	0.1044	0.0606	0.0622	0.0637
48.66	0.1011	0.1028	0.1044	0.0608	0.0623	0.0638
49.96	0.1011	0.1026	0.1040	0.0608	0.0622	0.0636
51.37	0.1005	0.1019	0.1031	0.0605	0.0619	0.0632
53.10	0.0988	0.0998	0.1005	0.0596	0.0607	0.0618
93.86	—	—	0.0023	—	—	—
96.93	0.0008	0.0009	0.0009	—	—	—
98.49	0.0004	0.0005	0.0006	—	—	—

are also set out in table III, as they give an important clue to the nature of the combination which is taking place in the mixture.

Another important matter bearing on this is the contraction which takes place at various constitutions of the mixture. The euthetic point, that is, the point of closest packing (see Bonsfield, T., 1915, 107, 1412), may be obtained by calculating the ratio of the volume of the constituents before mixture to the volume at the same temperature after mixture, which is

$$R = \frac{Pv_0 + (100 - P)v}{100v},$$

where  $v_0$ =specific volume of nitrogen peroxide,  $v$ =specific volume of nitric acid,  $v$ =specific volume of the mixture.

It should be noted that  $R - 1$  is the contraction per c.c. of solution formed, the values of which are set out in table IV.

In the same table are set out the values of the difference between the volume of a gram of the constituents before mixing and the volume after mixing, which is

$$\Delta = \frac{Pv_0 + (100 - P)v}{100} - v.$$

*Consideration of the Results.*—The results given in the tables are exhibited in Figs. 1, 2, 3, and 4, where they are set out on the values of  $P$ , the percentage by weight of nitrogen peroxide, as abscissæ. There are shown in:

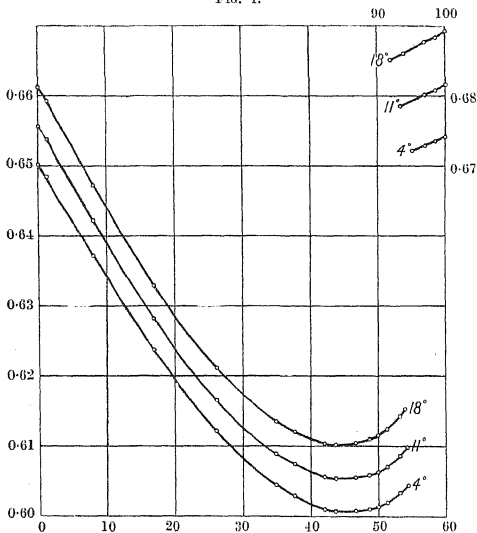
Fig. 1, the specific volumes of the mixtures.

Fig. 2, the values of  $R-1$  near the maximum.

Fig. 3, the values of  $\Delta$  near the maximum.

Fig. 4, the temperature coefficients for the intervals 4—11° and 11—18°.

FIG. 1.



Specific volume of mixtures of nitric acid and nitrogen peroxide at 4°, 11° and 18°.

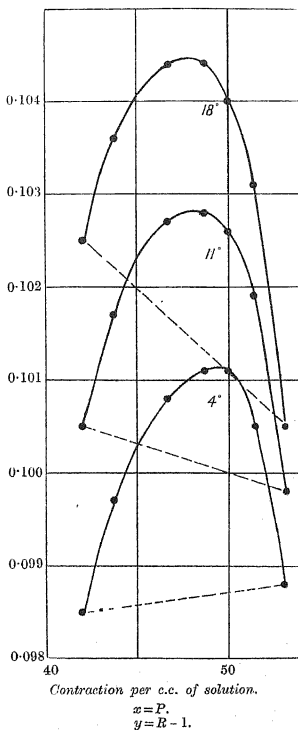
$x$  = Percentage of nitrogen peroxide.  
 $y$  = Specific volume.

The notable heat of evolution on mixing approximately equal weights of nitric acid and nitrogen peroxide (which it is proposed to determine accurately at a later stage) indicates a powerful combination. The minimum values of the specific volume curves give the same indication, showing a notable contraction of about 10

per cent. The minima do not, however, locate the exact composition. They occur:

for  $4^{\circ}$  at about 44.6 per cent.  
 for  $11^{\circ}$  „ 44.2 „  
 for  $18^{\circ}$  „ 43.8 „

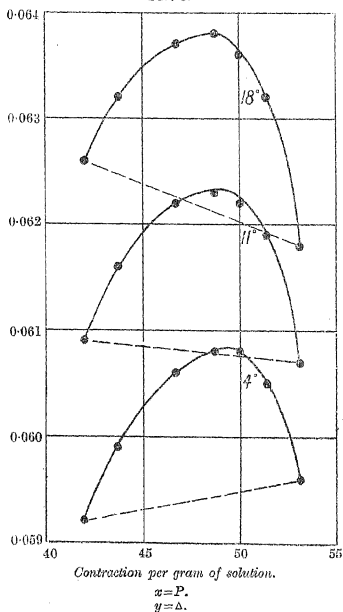
FIG. 2.



The position of the minimum is so largely determined by the mere density differences of the two components that it cannot locate precisely the percentage of the combination.

The euthetic point (see Bousfield, *loc. cit.*) is generally very close to the neighbourhood of the point of definite composition. The

FIG. 3.



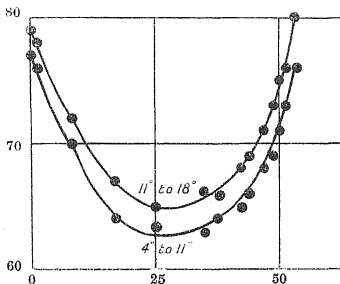
values of the contraction per c.c. of solution which determine the euthetic point are given in table IV and set out in Fig. 2. The maxima correspond with the euthetic point, and occur:

for 4°	at about 49.2 per cent.
for 11°	„ 48.4 „
for 18°	„ 47.6 „

The actual position of the euthetic point is determined, not only by contraction due to combination, but also by contraction due to changes in the polymerisation of the constituents. The high temperature coefficients for both constituents indicate that these changes are notable. The percentage 49.2 at  $4^{\circ}$  corresponds very nearly with the composition  $3\text{HNO}_3, 2\text{N}_2\text{O}_4$ .

If we take the curves in Fig. 3, in which the values of the contraction per gram of solution are set out, the effect of polymerisation is to some extent excluded, and the maxima for  $4^{\circ}$  and  $11^{\circ}$  appear to occur at 49.3 per cent., whilst that for  $18^{\circ}$  is again shifted slightly to the left. On the whole, then, it may be said

FIG. 4.



*Temperature-coefficients of specific volumes of mixtures of nitric acid and nitrogen peroxide.*

$x = P$ .

$y = \text{Temperature-coefficient } \alpha$ .

that the indications point to the composition of the definite compound  $3\text{HNO}_3, 2\text{N}_2\text{O}_4$ , which corresponds with 49.33 per cent.

An inspection of Fig. 4, in which the temperature coefficients are set out, shows a definite minimum at 26.7 per cent., which appears to be the same for each range of temperature; this corresponds with the definite composition  $4\text{HNO}_3, \text{N}_2\text{O}_4$ . The first part of the specific volume curve shown in Fig. 1 is approximately straight, which indicates that the whole of the nitrogen peroxide added up to about 15 per cent. enters into this combination with nitric acid. Furthermore, the proportions of nitric acid and the compound,  $4\text{HNO}_3, \text{N}_2\text{O}_4$ , derived from the mass-action relation give a calculated specific volume which corresponds closely with

the actual specific volume curve for a considerable distance, that is, until the effect of the increasing proportion of the still denser combination becomes sensible. On the whole, we may conclude that at least two definite compounds exist in the solutions, namely,  $4\text{HNO}_3 \cdot \text{N}_2\text{O}_4$  and  $3\text{HNO}_3 \cdot 2\text{N}_2\text{O}_4$ .

*The Composition of the Double Layers.*—The specific volume curves have a gap between about 54 and 92 per cent. If at  $4\text{--}18^\circ$  a mixture between these limits is made, the solution separates into two layers, which are mutually saturated.

Nitrogen peroxide is soluble in nitric acid up to about a 54 per cent. solution, but the solubility of nitric acid in nitrogen peroxide is very much less. In order to determine the maximum solubilities at different temperatures, the two components were shaken together from time to time at the required temperatures, forming a cloudy liquid, and kept in a thermostat until the two clear layers were completely separated. The different layers were then drawn off into a pyknometer at the required temperatures, and again kept in the thermostat at these temperatures during the adjustment of the pyknometer. The resulting density determinations enabled the compositions to be determined.

In table V are given the density observations for saturated solutions of nitric acid in nitrogen peroxide, together with the specific volumes at the temperatures and the resulting percentage,  $p$ , of nitric acid in the saturated solutions.

TABLE V.

*Saturated Solutions of Nitric Acid in Nitrogen Peroxide.*

	D.	$v$ .	Percentage of nitric acid.
$4^\circ$	1.48742	0.67231	4.90
11	1.47351	0.67865	6.67
18	1.45940	0.68521	8.05

Since at this end of the specific volume curves they are practically straight lines, the percentages are easily calculated from the formula

$$v_0 - v_1 = \beta p,$$

where  $v_0$  = specific volume of nitrogen peroxide,  $v_1$  = specific volume of solution containing  $p$  per cent. of nitric acid, the values of the constants being:

	$4^\circ$ .	$11^\circ$ .	$18^\circ$ .
$v_0$	0.67435	0.68172	0.68938
$\beta$	0.000424	0.000476	0.000526

It will be observed that the solubility of nitric acid in nitrogen peroxide rises rapidly with temperature, being about doubled in



the range from  $0^{\circ}$  to  $20^{\circ}$ . The values indicate that the solubility would vanish at about  $-10^{\circ}$ .

In table VI are given the density observations for saturated solutions of nitrogen peroxide in nitric acid, together with the specific volume at the temperatures and the approximate percentages of nitrogen peroxide in the saturated solutions.

TABLE VI.

*Saturated Solutions of Nitrogen Peroxide in Nitric Acid.*

	D.	v.	P.
$4^{\circ}$	1.65432	0.60448	54.4
11	1.63942	0.60997	54.3
18	1.62501	0.61538	54.0

In this case, the approximate compositions are determined diagrammatically from a large-scale specific volume curve. The temperature of my laboratory in the end of May when these last observations were taken made them very difficult. It is, however, clear that the change of solubility with temperature is in this case very small, and it appears to diminish with rising temperature.

ST. SWITHIN'S,  
HENDON, N.W.

[Received, August 29th, 1918.]

#### IV.—*The Effect of Dilution in Electro-titrimetric Analyses.*

By GILBERT ARTHUR FREAK.

THE first application of conductivity measurements to analysis is that due to Küster and Grüters (*Zeitsch. anorg. Chem.*, 1903, **35**, 454), who showed that acids could be titrated accurately by these means. Later, Küster, Grüters, and Geibel (*ibid.*, 1904, **42**, 225) proved the accuracy of the method even when such substances as potassium dichromate and potassium permanganate were present in the acid solution. The estimation of acetic acid in vinegar, of total acid in red wine, of magnesia, and of various alkaloids was also shown to be possible.

Further work has demonstrated that the method is capable of very varied application. Amongst the uses to which it has been put may be noticed the analysis of wines by Duboux (*Chem. Zeit.*, 1913, **37**, 879) and by Duboux and Dutoit (*Compt. rend.*, 1908,

147, 134), the preparation of neutral ammonium citrate solutions by Hall (*J. Ind. Eng. Chem.*, 1911, **3**, 559), and the analysis of soil solutions by Van Suchtelen and Itano (52nd *Ann. Rep. Mich. Board of Agric.*, 1913, 49). The last-named workers have also published (*J. Amer. Chem. Soc.*, 1914, **36**, 1793) the results of experiments on the estimation of chlorides, sulphates, nitrates, phosphates, potassium, calcium, ferrous iron, strong and weak acids, and of chlorides and phosphates in urine. Quite recently, Harned (*J. Amer. Chem. Soc.*, 1917, **39**, 252) has shown that certain bivalent metals in the form of their sulphates can be determined accurately by the conductivity method by titration with barium hydroxide. Meerburg (*Versl. v. h. Centr. Lab. t. b. h. v. h. Staatsoez. o. d. Volksgebondh.*, 44-54, 1917; *Chem. Weekblad*, 1917, **14**, 1054) has reported adversely on the method as applied to the estimation of sulphates by barium acetate and of calcium by oxalic acid, but mentions that good results may be obtained in the determination of alkalinity in potable waters.

It is noteworthy that, although the method has been applied to so many reactions, no attention has been paid to the lower limit of concentration at which accuracy may still be obtained. Most of the experiments have been carried out on relatively concentrated solutions (seldom weaker than 0.1*N*), the only reference to results with very dilute solutions being one by Van Suchtelen and Itano (*loc. cit.*), who state that the titration of as little as 5 c.c. of 0.001*N*-sulphuric acid with 0.01*N*-sodium hydroxide can be performed accurately. In those titrations involving the precipitation of a salt, the solubility of which would be expected to limit the sensitiveness of the method, this point has not been touched upon.

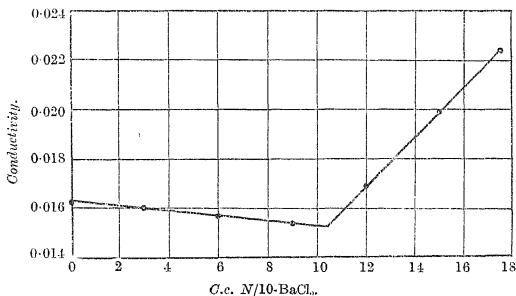
It appears, therefore, to the author that an investigation of this nature was desirable. If the method is capable of yielding accurate results at very low concentrations, many estimations, for example, those carried out in the analysis of potable waters, could be made without previous concentration of the solutions. The present communication is concerned with the limits of the method as applied to the estimation of sulphates, chlorides, calcium, and magnesium. Rigid accuracy was not aimed at, the object being to find to what extent the method could compete with ordinary gravimetric or volumetric processes without the introduction of troublesome precautions. To that end, beyond the use of standardised measuring vessels and of "purest" commercial reagents, no special precautions were taken. No attempt was made to keep the temperature of the solutions constant during the titrations, the duration of which was usually fifteen to twenty minutes.

## EXPERIMENTAL.

Except for the use of a double receiver telephone, which proved very convenient in minimising the interference of external noises, the apparatus employed was of the usual nature and therefore calls for no special comment.

The liquid to be titrated was placed in a beaker of such a size that thorough mixing could be effected by giving the vessel a rotatory motion, the stationary electrodes serving as a stirrer. The reagent was delivered from a burette capable of being read to 0.01 c.c. The curves were plotted with conductivity as ordinates and volume

FIG. 1.



of reagent as abscissæ, and in order to eliminate experimental errors at least three, and usually more, readings were taken on each limb of the curve.

*Estimation of Sulphates.*

A stock solution of Merck's purest potassium sulphate was prepared and the  $\text{SO}_4$  estimated gravimetrically in duplicate as barium sulphate. From this solution weaker solutions were prepared by dilution. For the titration of these, two solutions of barium chloride, approximately  $N/10$  and  $N/25$  respectively, were prepared and similarly standardised.

Table I shows that the results are accurate only down to a concentration of about 200 milligrams of  $\text{SO}_4$  per litre, a typical curve being shown in Fig. 1. When the concentration of  $\text{SO}_4$  is 100 milli-

grams or less per litre, the precipitation of barium sulphate is so incomplete that the resulting curve changes entirely in character, exhibiting irregularity, but no definite break such as appears in Fig. 1.

Van Suchtelen and Itano (*loc. cit.*) added to their solutions a certain amount of the salt that was to be precipitated with the object of avoiding errors due to solubility. In order to test this procedure, a suspension of fine precipitated barium sulphate in distilled water was added to the sulphate solution in the beaker some little time prior to titration. The results are given in Table II.

TABLE I.

Concentration of $\text{SO}_4$ , mg. per litre.	Strength of $\text{BaCl}_2$ .	$\text{SO}_4$ found. Per cent.
990	N/10	100.0, 100.4, 99.4
198	"	99.2, 99.2, 99.2
99	N/25 }	No end-point.
49.5		

TABLE II.

Concentration of $\text{SO}_4$ , mg. per litre.	Strength of $\text{BaCl}_2$ .	$\text{SO}_4$ found. Per cent.
99	N/10	99.7, 99.7
49.5	N/25	99.5, 99.2, 99.6
24.7	" }	End-point indefinite.
9.9		

Reference to table II will show that this method succeeded to a certain extent as, by means of it, good results were obtained down to a concentration of about 50 milligrams of  $\text{SO}_4$  per litre. However, it was not effective when only 25 milligrams of  $\text{SO}_4$  per litre were present, giving curves with an indefinite end-point of the type shown in Fig. 2. Titration at boiling temperature did not alter the character of this curve. In such cases it is possible, by taking only those points well remote from the curved portion, to arrive at an approximate value for the end-point (see dotted lines). For instance, figures derived in this manner from experiments on solutions containing 25 milligrams of  $\text{SO}_4$  per litre were about 5 per cent. in excess of the correct value.

#### *Estimation of Chlorides.*

The salt chosen for this purpose was a sample of Merck's purest fused sodium chloride. A stock solution of this, together with the approximately N/10- and N/25-silver nitrate solutions used for titration, was standardised by duplicate gravimetric estimations as silver chloride.

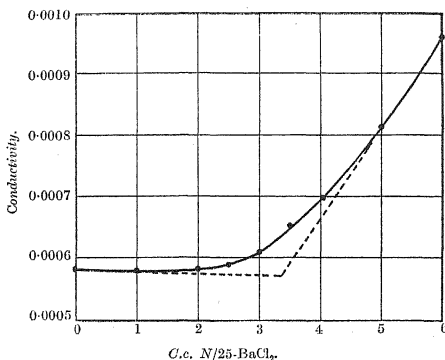
The results obtained with varying concentration of chlorine are shown in table III.

TABLE III.

Concentration of Cl, mg. per litre.	Strength of AgNO <sub>3</sub> .	Cl found. Per cent.
1000	N/10	99.7, 99.3
200	"	100.1, 99.3, 100.8
50	N/25	100.2, 100.9
10	"	100.6, 100.8
5	"	End-point indefinite.

As in the case of sulphates, a limit of concentration is reached at which the method fails, the figure in this instance being 10 milli-

FIG. 2.



grams of chlorine per litre. The addition of precipitated silver chloride before titration did not render the end-point sharp at lower concentrations.

The type of curve obtained in this estimation is similar to that shown in Fig. 1.

#### *Estimation of Calcium.*

A stock solution of calcium chloride was prepared by dissolving pure calcite in hydrochloric acid and eliminating the excess of acid by repeated evaporations on the water-bath. Both this solution and the approximately N/10-ammonium oxalate solution employed

in the titrations were standardised by means of potassium permanganate.

Table IV shows the results obtained.

TABLE IV.

Concentration of Ca, mg. per litre.	Ca found. Per cent.
500	100.0, 100.4, 99.2, 100.4
200	99.1, 100.6, 99.1
100	End-point indefinite.

As in the case of the determination of chlorides, previous addition of the precipitated salt did not lead to sharp end-points at the last-mentioned concentration. In three such experiments, figures given by producing the straight portions of the curves gave 97.0, 97.6, and 95.8 per cent. respectively of the amounts taken.

#### *Estimation of Magnesium.*

A solution of Merck's purest magnesium sulphate was employed, standardisation being effected by duplicate estimations as magnesium pyrophosphate. An approximately *N*/10-sodium hydroxide solution, standardised by means of sulphuric acid and pure sodium carbonate, was used for titration.

Variation of the concentration of magnesium gave results shown in table V. The typical curves for these cases have no minimum, but exhibit a definite break.

TABLE V.

Concentration of Mg, mg. per litre.	Mg. found. Per cent.
539	99.2, 99.7, 99.7
269.5	99.7, 100.1, 100.4, 100.1
202	100.8, 99.9, 100.8, 100.6
134.5	End-point indefinite.

Addition of magnesium hydroxide prior to titration lead to no improvement at the last-mentioned concentration.

In connexion with the estimation of magnesium by this method it is interesting to note that Harned (*loc. cit.*) says, "This titration gives only a fairly easily detectable end-point for the change in direction of the plot before and after the end-point is not great. A reagent must, therefore, be sought which will increase the difference in the slopes at the end-point." For this reason he employed barium hydroxide to titrate solutions containing magnesium sulphate. Apart from the fact that the use of this reagent, to be

effective, demands that the magnesium shall be present as sulphate and the total elimination of carbon dioxide from the solution, comparison of Harned's figures with those recorded above shows that the use of barium hydroxide does not present any definite advantage. It appears that errors from other sources are of greater magnitude than that derived from difficulty in reading the intersection of the two limbs of the curve.

### *Summary of Results.*

(1) The determination, by means of conductivity measurements, of sulphates, chlorides, calcium, and magnesium has been studied at low concentrations.

(2) It has been shown that, in relatively weak solutions, very small quantities of each of the above mentioned may be estimated, without any attempt at temperature control, with an error not exceeding  $\pm 1$  per cent.

(3) In each case a limit of dilution is reached at which the results cease to be accurate, smooth conductivity curves being obtained. With the exception of the case of sulphate estimations, saturation of the solution with the salt to be precipitated does not lead to an improvement in this respect.

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[Received, August 6th, 1918.]

## V.—*The Optically Active neoMethylhydrindamines.*

By (the late) LT. JOSEPH WALTER HARRIS.\*

THE reduction of  $\beta$ -methyl- $\alpha$ -hydrindoxime,  $\text{CH}_2\text{CH}(\text{CHMe})\text{C}(\text{NOH})$ , with sodium amalgam and acetic acid leads to the formation of two

\* Lt. J. W. Harris, B.Sc., was one of those who, actuated by a high sense of patriotic duty, joined the O.T.C. of the University College, Nottingham, before there was any immediate prospect of a war, and his efficiency and enthusiasm led to his promotion to the rank of colour sergeant. In the summer of 1914 he had just completed his first piece of research work and when war was declared he immediately volunteered for active service. Shortly afterwards he was given a commission in the 3rd Lincolns and went to the Western front, where he was killed in action during the early part of the war.

His death was a great blow to all who knew him, whether in civilian or in military life; he was a most promising chemist, an ideal officer. The present

*dl*-bases, one of which may be isolated by the fractional crystallisation of the hydrochlorides prepared from the mixture (Kipping and Clarke, T., 1903, **83**, 913). The other base cannot be obtained, at any rate easily, in this way or by a similar treatment of the normal sulphates, benzoates, cinnamates, or picrates, but by fractionally crystallising the *d*-bromocamphorsulphonates and mechanically separating the obviously different crystals, both the *dl*-bases can be ultimately obtained in a state of purity (Tattersall and Kipping, T., 1903, **83**, 918).

As this method of separation was unsatisfactory, the author of this paper, at the suggestion of Professor Kipping, made some further experiments on the subject, and found that the two *dl*-bases in the crude product could be isolated in the manner described below. He then succeeded in resolving the *dl-neo*-base into its optically active components, both of which were obtained in a state of purity.

All the four optically isomeric  $\beta$ -methylhydrindamines, therefore, have now been characterised; the two *neo*-bases, which form only about 25 per cent. of the original mixture, have very low molecular rotations compared with those of the other two methylhydrindamines.

*Separation of Methylhydrindamine and neoMethylhydrindamine  
by means of their Hydrogen Oxalates.*

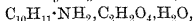
The aqueous solution of the mixed bases obtained by the reduction of methylhydrindoxime was neutralised with finely divided oxalic acid, and a further equal quantity of acid was added. This solution was then concentrated and cooled. The first fraction consisted of tufts of long, silky needles, and was nearly pure methylhydrindamine hydrogen oxalate. Subsequent fractions were similar, but the needles gradually became less well defined, and when about two-thirds of the total substance had been separated the deposits consisted of hard, crystalline masses. The latter, after several recrystallisations from water, yielded tufts of needle-like prisms which were *neomethylhydrindamine* hydrogen oxalate. Some ammonium salts separated in large, transparent masses from time to time, but these were easily removed by extracting the salt of the organic base with alcohol. By the above method about five-sixths of the original mixture was separated into the two *dl*-salts, the pro-

paper is an account of his work, which he handed to me before he went to the front, and except the few lines of introduction and some immaterial alterations, the matter is given in his own words.—F. S. K.



portion being about three to one, methylhydrindamine being present in the larger quantity.

*dl-Methylhydrindamine hydrogen oxalate,*



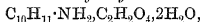
crystallises from water, in which it is readily soluble, in tufts of long, silky needles melting at 110—111°. These are hydrated and lose water at 70—80°; at 100° some decomposition is observed, but this is not noticeable in the melting-point tube. The dehydrated salt melts at 143—145° with slight decomposition:

0.4338 lost 0.031 at 80°.  $\text{H}_2\text{O}=7.14$ .

The above formula requires  $\text{H}_2\text{O}=7.06$  per cent.

The benzoyl derivative of the base, made in the usual way, crystallised from alcohol in needles melting at 150°, showing the base to be methylhydrindamine (Tattersall and Kipping, *loc. cit.*).

*dl-neoMethylhydrindamine hydrogen oxalate,*



in an impure condition, crystallises in compact masses. From water and alcohol the pure compound is obtained in tufts of needle-like prisms, which partly liquefy at about 100° and finally melt at 173—175°, which is the melting point of the anhydrous salt. When treated with benzoyl chloride, the salt gave a benzoyl derivative, crystallising in needles and melting at 169°, which is the melting point of the benzoyl derivative of *neomethylhydrindamine* (Tattersall and Kipping, *loc. cit.*): \*

0.4336 lost 0.0568 at 90°.  $\text{H}_2\text{O}=13.1$ .

The above formula requires a loss of 13.2 per cent.

0.1454 anhydrous salt gave 0.3246  $\text{CO}_2$  and 0.0834  $\text{H}_2\text{O}$ ;  $\text{C}=60.8$ ;  $\text{H}=6.4$ .

$\text{C}_{12}\text{H}_{15}\text{O}_4\text{N}$  requires  $\text{C}=60.8$ ;  $\text{H}=6.33$  per cent.

#### *Resolution of dl-neoMethylhydrindamine.*

*dl-neoMethylhydrindamine hydrogen oxalate* (20 grams) was decomposed with sodium hydroxide, the base distilled in steam, and the distillate neutralised with tartaric acid, a further equal quantity of the acid being added to form the hydrogen salt. The solution was then concentrated to a small bulk, allowed to cool, and a crystal of pure *l-neomethylhydrindamine* hydrogen tartrate intro-

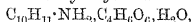
\* Since the melting point of the *A*-base described by Kipping and Clarke (*loc. cit.*) was 169°, it is evident that by the fractional crystallisation of the hydrochlorides of the mixed bases, the salt of *dl-neomethylhydrindamine* is first isolated, whereas in the case of the *d*-bromocamphorsulphonates the salt of *dl-methylhydrindamine* forms the most sparingly soluble fraction.—  
F. S. K.

duced. A deposit consisting of tufts of needles separated and was collected. The amount of this fraction was roughly about one-third of the whole. If the solution was allowed to remain too long before it was filtered, the needle-like crystals became covered with white masses. This first fraction was recrystallised from water until its melting point became constant and consisted of *l*-neomethylhydrindamine hydrogen tartrate (about 8 grams). The mother liquors, on further concentration and seeding, gave deposits of white masses, obviously a mixture and melting over a wide range. The last mother liquors gave long, white needles melting at 165°. It was, however, found to be impossible to isolate a pure compound from these mother liquors, owing to the great solubility of the salt.

The whole of the mother liquor was therefore decomposed with sodium hydroxide, the base distilled in steam, and the distillate neutralised with hydrochloric acid. On concentrating the solution, long needles of *dl*-neomethylhydrindamine separated, but the final mother liquor was found to contain a salt which was more readily soluble in water than that of the *dl*-base, and the solution of this salt showed dextrorotation.

To obtain this dextrorotatory base, the active mother liquor was decomposed with sodium hydroxide, the base distilled in steam, and the solution neutralised with *d*-bromocamphorsulphonic acid. The solution was concentrated until it became turbid and allowed to remain, when a mass of needles separated. These were recrystallised from water until the melting point became constant at 229–230°. This substance was found to be *d*-neomethylhydrindamine *d*'bromocamphorsulphonate.

*l*-neomethylhydrindamine hydrogen tartrate,



the salt which forms the most sparingly soluble portion described above, crystallises from water or alcohol in large, vitreous prisms, often growing together in leaf-like masses. It is hydrated, and when heated in a melting-point tube it partly liquefies at about 100° and finally melts at 173°. It is readily soluble in water, less so in alcohol, and practically insoluble in ethyl acetate, acetone, benzene, or chloroform:

0.3522 lost 0.0204 at 100°.  $\text{H}_2\text{O}=5.71$ .

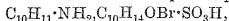
The above formula requires  $\text{H}_2\text{O}=5.71$  per cent.

Samples dried at 100° gave, in a 200 mm. tube in aqueous solution, the following results:

Wt. of salt.	Vol. of solution.	$\alpha$ .	$[\alpha]_D$ .	$[M]_D$ .
0.7116 gram .....	25 c.c.	0.65°	11.4°	34°
0.4600 " .....	"	0.42	11.4	34

As the molecular rotation of the tartaric acid ion in its metallic hydrogen salts is  $[M]_D 42^\circ$ , that of the base is  $[M]_D -8^\circ$ .

*l-neoMethylhydrindamine d-bromocamphorsulphonate*,



is moderately soluble in water, and crystallises from the warm solution in aggregates of needles, the solution first becoming milky if the salt is not free from the optically active isomeric base. These needles are hydrated, but lose all their water on exposure to the air. The freshly crystallised substance when heated in a melting-point tube partly liquefies at about  $80^\circ$  and finally melts at  $214^\circ$ . It is more readily soluble in alcohol than in water, and easily dissolves in ethyl acetate, chloroform, or acetone, but is insoluble in ether.

The anhydrous salt was examined in aqueous solution in a 200 mm. tube.

Wt. of salt.	Vol. of solution.	$\alpha$ .	$[\alpha]_D$ .	$[M]_D$ .
0.5068 .....	25 c.c.	$2.32^\circ$	$57.2^\circ$	$262^\circ$
0.3856 .....	„	$1.75$	$57.1$	$261$

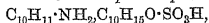
Taking the molecular rotation of the bromocamphorsulphonic acid ion to be  $[M]_D 270^\circ$ , these results give a value of  $[M]_D -8^\circ$  or  $-9^\circ$  for the base.

*l-neoMethylhydrindamine hydrochloride*,  $C_{10}H_{11}\cdot NH_2\cdot HCl$ , is much more readily soluble in water than the hydrochloride of the *dl*-base, and crystallises from this solvent in long, silky needles. It is very readily soluble in water or alcohol and also dissolves in ethyl acetate or chloroform, but is practically insoluble in ether or carbon tetrachloride. When heated in a melting-point tube, the substance begins to char at about  $235^\circ$ . The air-dried salt is anhydrous.

The following results were obtained in aqueous solution in a 200 mm. tube:

Wt. of salt.	Vol. of solution.	$\alpha$ .	$[\alpha]_D$ .	$[M]_D$ .
0.5250 .....	25 c.c.	$-0.13^\circ$	$-3.1^\circ$	$-5.7^\circ$
0.7986 .....	„	$-0.23$	$-3.6$	$-6.5$
0.7754 .....	„	$-0.21$	$-3.4$	$-6.2$

*l-neoMethylhydrindamine d-camphorsulphonate*,



is very readily soluble in water, and crystallises in long, vitreous prisms. The air-dried salt is anhydrous, and when heated sinters at about  $210^\circ$  and finally melts at  $220^\circ$ . It is readily soluble in chloroform, sparingly so in alcohol or acetone, and practically insoluble in ether or ethyl acetate.

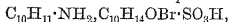
The following results were obtained in aqueous solution in a 200 mm. tube:

Wt. of salt.	Vol. of solvent.	$\alpha$ .	$[\alpha]_D$ .	$[M]_D$ .
0.5898 .....	25 c.c.	0.54°	11.4°	43.2°
0.5282 .....	„	0.50	11.8	44.7

Taking  $[M]_D$  for camphorsulphonic acid as 49°, these results give for the base  $[M]_D$   $-5.8^\circ$  and  $-4.3^\circ$  respectively.

The *benzoyl* derivative of *l*-neomethylhydrindamine crystallises from aqueous alcohol in long, silky needles melting at 171°.

*d*-neoMethylhydrindamine *d*-bromocamphorsulphonate,



is readily obtained in a pure condition from the active base contained in the mother liquors from the *dl*-hydrochloride (see above). It crystallises from warm water in tufts of fine, silky needles, and, as with many other bromocamphorsulphonates, the warm solution becomes milky when the salt separates unless it is free from its optical isomeride. The freshly crystallised salt contains water, probably one molecular proportion, but it was impossible to obtain accurate determinations on this point, since the salt rapidly loses water in the air and the air-dried salt is anhydrous.

1.69 of the salt, roughly dried in the air, lost 0.544 at 100°.

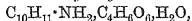
Loss = 3.2, whereas  $1H_2O$  requires a loss of 3.1 per cent.

When the freshly crystallised salt is heated in a melting-point tube it partly liquefies at about 100° and finally melts at 229—230°. It is moderately soluble in water, more readily so in alcohol; it is also soluble in acetone or ethyl acetate, but insoluble in carbon tetrachloride or ether.

*d*-neoMethylhydrindamine hydrochloride,  $C_{10}H_{11} \cdot NH_2 \cdot HCl$ , prepared from the pure bromocamphorsulphonate, was dried at 100° and examined polarimetrically in aqueous solution in a 200 mm. tube.

Wt. of salt.	Vol. of solution.	$\alpha$ .	$[\alpha]_D$ .	$[M]_D$ .
0.5200 .....	25 c.c.	0.13°	3.1°	5.7°
0.4268 .....	„	0.10	3.0	5.5

*d*-neoMethylhydrindamine hydrogen tartrate,



is much more readily soluble in water than the hydrogen tartrate of the *l*-base, and crystallises in aggregates of needle-like prisms:

1.2146 air-dried salt lost 0.0726 at 100°.  $H_2O = 5.9$ .

The above formula requires  $H_2O = 5.71$  per cent.

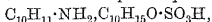
When heated in a melting-point tube the salt sinters at about 90° and finally melts at 166—167°. The following results were

obtained with aqueous solutions of the anhydrous salt in a 200 mm. tube :

Wt. of salt.	Vol. of solution.	$\alpha$ .	$[\alpha]_D$ .	$[M]_D$ .
0.3122 .....	25 c.c.	0.40°	16.0°	47.5°
0.3328 .....	„	0.43	16.2	48.1

Taking the molecular rotation of the tartaric acid ion in its hydrogen salts as  $[M]_D 42^\circ$ , these results give  $[M]_D 5.5^\circ$  and  $6.1^\circ$  respectively for the base.

d-neoMethylhydrindamine d-camphorsulphonate,



crystallises from water in felted masses of needles which melt and decompose at  $195-205^\circ$ . The salt is extremely readily soluble in water and readily so in alcohol or chloroform. It is sparingly soluble in ethyl acetate and practically insoluble in ether.

A sample dried at  $100^\circ$  examined in aqueous solution in a 200 mm. tube gave the following result: 0.6176 gram in 25 c.c. of solution gave  $\alpha 0.73^\circ$ ,  $[\alpha]_D 14.8^\circ$ ,  $[M]_D 56.1^\circ$ . Taking the molecular rotation of the acid ion as  $49^\circ$ , that of the base is  $[M]_D 7^\circ$ .

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## VI.—Chromatocobaltiammines.

By SAMUEL HENRY CLIFFORD BRIGGS.

PREVIOUS investigations have shown that the chromate radicle possesses considerable residual affinity, and has a strongly marked tendency to form complex salts (Briggs, *Zeitsch. anorg. Chem.*, 1907, **56**, 246; 1909, **63**, 325; Groeger, *ibid.*, 1908, **58**, 412). It was therefore to be expected that the chromatocobaltiammines would be a well-defined and stable class of substances, containing one or more non-ionisable chromate radicles. As soluble compounds containing a non-ionisable chromate radicle have not previously been described, the study of the chromatocobaltiammines was undertaken in order to compare the properties of the chromate radicle in non-ionisable combination with those of the ionisable radicle in the ordinary chromates.

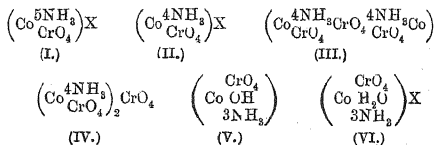
The chromatocobaltiammines are readily prepared by the action of potassium chromate on the corresponding aquo-compounds in solution. Thus, when a solution of potassium chromate is added to a warm solution of an aquopentamminecobaltic salt, a chromato-

pentamminecobaltic salt (I) crystallises out on cooling. The *nitrate*, *chloride*, and *chromate* of this series were obtained in a pure condition.

The chromatotetramminecobaltic salts (II) are formed in a similar manner, and the *chromate*, *dichromate*, and *nitrate* were prepared in a pure state. When a solution of a diaquotetramminecobaltic salt is treated with an excess of potassium chromate, *trichromato-octamminedicobalt* (III) crystallises out on keeping. Trichromato-octamminedicobalt is isomeric with chromatotetramminecobaltic chromate (IV), but the two compounds are very different. The former is almost completely insoluble in water, and forms greenish-black crystals containing five molecules of water of crystallisation, whilst the latter is obtained as a greenish-brown precipitate with three molecules of water of crystallisation; it is moderately soluble in water, and its solution gives the reactions of the chromate ion.

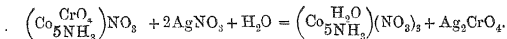
Attempts to prepare chromatotriammine compounds by the action of potassium chromate on triaquotriamminecobaltic nitrate were not successful, the product being chromatohydroxotriamminecobalt (V), which, however, was not obtained in a completely pure condition. It therefore appears that when more than two molecules of ammonia in the hexamminecobaltic radicle are replaced by the chromate radicle, the products are unstable in the presence of water, and undergo hydrolysis. This explains why endeavours to prepare potassium cobaltic chromate,  $K_3Co(CrO_4)_3$ , by oxidising cobaltous salts in the presence of potassium chromate, failed, cobaltic hydroxide and potassium dichromate being obtained. The formation of chromatohydroxotriamminecobalt in the above manner also supports the view that the basic chromates are hydroxo-compounds in accordance with Werner's theory of basic salts ("Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 3rd ed., pp. 177-178).

Some evidence was obtained which pointed to the existence of a chromatoaquotriammine series (VI), a compound being prepared which had the composition of chromatoaquotriamminecobaltic dichromate:



In the chromatopentammine- and chromatotetrammine-cobaltic salts the chromate radicle in the complex is non-ionisable, no pre-

cipitate being obtained when silver nitrate is added to cold, freshly prepared solutions of the pure nitrates. If the mixture is allowed to remain for some time, however, silver chromate is slowly deposited, showing that the chromato-salts have a tendency to pass into the corresponding aquo-salts as seen from the equation:



If the solution is heated the change takes place at once, and silver chromate is immediately precipitated.

The chromate radicle in these compounds reacts with hydrogen ions in the same way as in the ordinary chromates. When an acid is added to a solution of a chromatopentammine or chromatotetrammine salt, the complex is decomposed, as seen from the change in colour of the solution.

In the chromatopentammine salts the chromate radicle fills one co-ordination position according to Werner's theory, whereas in the chromatotetrammine salts it fills two positions.

The entrance of the chromate radicle into the complex is accompanied by marked intensification of colour, and all the chromatocobaltammines are deeply coloured substances.

## EXPERIMENTAL.

### *Pentammine Series.*

*Chromatopentamminecobaltic Nitrate*,  $\left(\text{Co}_5\text{NH}_3\right)\text{CrO}_4\text{NO}_3$ .—Carbonatopentamminecobaltic nitrate was converted into aquopentamminecobaltic nitrate, and potassium chromate was then added to the solution, the details of the preparation being as follows.

Carbonatopentamminecobaltic nitrate (2.5 grams) was dissolved in 100 c.c. of water, a little dilute nitric acid was added, and the solution was gently warmed to expel carbon dioxide. The liquid was then just neutralised by potassium hydroxide, diluted to 300 c.c., and heated to 60–70°. One and a-half grams of potassium chromate in 100 c.c. of water also heated to 60–70° were added, and the clear solution was allowed to crystallise. The chromatopentamminecobaltic nitrate separated in brownish-red, acicular crystals (2.2 grams), which were collected, washed with a little water, and dried in the air.

Found: Co=18.51; CrO<sub>3</sub>=31.74; NH<sub>3</sub>=26.36.

$\left(\text{Co}_5\text{NH}_3\right)\text{CrO}_4\text{NO}_3$  requires Co=18.35; CrO<sub>3</sub>=31.05; NH<sub>3</sub>=26.44 per cent.

The salt was moderately soluble in cold water, and the freshly

prepared solution was not precipitated by silver, lead, or barium salts, but precipitation took place at once on heating. The chromate radicle is therefore situated in the complex, as shown by the above formula, and the salt is isomeric with Jörgensen's nitratopentamminecobaltic chromate,  $(\text{Co}^{5\text{NH}_3}_{\text{NO}_3})\text{CrO}_4$  (*J. pr. Chem.*, 1881, [ii], 23, 245).

*Chromatopentamminecobaltic Chloride*,  $(\text{Co}^{5\text{NH}_3}_{\text{CrO}_4})\text{Cl}$ .—Chloropentamminecobaltic chloride was converted into aquopentamminecobaltic chloride by Werner's method (*Ber.*, 1907, 40, 4104), and this was treated with potassium chromate.

Twenty-five grams of chloropentamminecobaltic chloride were heated with 625 c.c. of water and 62.5 c.c. of concentrated aqueous ammonia until the chloride was completely dissolved. After cooling, the liquid was just neutralised with hydrochloric acid, and heated to 60°. Sixteen grams of potassium chromate in 500 c.c. of water, also heated to 60°, were then added, and the mixture was allowed to cool. After crystallisation was complete, the salt was collected, washed with a little water, and dried in the air. Twenty-three grams of brownish-red crystals (*A*) were thus obtained. The mother liquor was heated to 50° and 4 grams of potassium chromate dissolved in a little water were added. On cooling, 1.2 grams of a second salt (*B*) were obtained in yellowish-brown prisms, almost insoluble in cold water, but readily soluble on warming to give a yellow solution. The salt *A* was anhydrous, but *B* contained water of crystallisation; otherwise the salts were similar in composition, as seen from the analyses:

*A*. Found: Co=19.86;  $\text{CrO}_3$ =33.97, 34.27; Cl=12.02;  $\text{NH}_3$ =27.30, 27.15, 27.08.

$(\text{Co}^{5\text{NH}_3}_{\text{CrO}_4})\text{Cl}$  requires Co=19.96;  $\text{CrO}_3$ =33.83; Cl=12.00;  $\text{NH}_3$ =28.81 per cent.

*B*. Found: Co=16.91; Cl=9.80;  $\text{CrO}_3$ =29.94;  $\text{NH}_3$ =26.6;  $\text{H}_2\text{O}$ =13.95.

$2(\text{Co}^{5\text{NH}_3}_{\text{Cl}})\text{CrO}_4 \cdot 5\text{H}_2\text{O}$  requires Co=17.31; Cl=10.41;  $\text{CrO}_3$ =29.36;  $\text{NH}_3$ =25.0;  $\text{H}_2\text{O}$ =13.22 per cent.

The solution of the salt *A* on addition of silver nitrate gave a copious precipitate. This was filtered off, and on treatment with dilute nitric acid was found to consist of silver chloride coloured by the presence of a trace of silver chromate. The reddish-yellow filtrate, on heating, deposited a precipitate of silver chromate. The



salt *A* was therefore *chromatopentamminecobaltic chloride*,  
 $(\text{Co}_{5\text{NH}_3}^{\text{CrO}_4})\text{Cl}$ .

The solution of the salt *B* on addition of silver nitrate gave a red precipitate, which was filtered off, the filtrate being only faintly coloured. The precipitate consisted of silver chromate. It dissolved in dilute nitric acid, leaving only a trace of silver chloride. The salt *B* was therefore a hydrated *chloropentamminecobaltic chromate*,  $2(\text{Co}_{5\text{NH}_3}^{\text{Cl}})\text{CrO}_4 \cdot 5\text{H}_2\text{O}$ .

Various preparations of the salt *A* (*chromatopentamminecobaltic chloride*) were made, but in all cases the ammonia content was low. The salt could not be purified by crystallisation from hot water, as it was then found to contain a little of the corresponding chromate,  $(\text{Co}_{5\text{NH}_3}^{\text{CrO}_4})\text{CrO}_4$ , which is very sparingly soluble in water. The reason for the low percentage of ammonia could not be ascertained, and this is all the more remarkable as the salt, on treatment with silver chromate, gave the corresponding chromate in a high degree of purity.

*Chromatopentamminecobaltic Chromate*,  $(\text{Co}_{5\text{NH}_3}^{\text{CrO}_4})\text{CrO}_4 \cdot 3\text{H}_2\text{O}$ .

—Two grams of silver nitrate were precipitated in the cold with 1 gram of potassium chromate, and the precipitate was washed two or three times by decantation. The supernatant liquid was separated as far as possible by decantation, and the precipitate was then poured into a solution of 3 grams of *chromatopentamminecobaltic chloride* in 150 c.c. of water at 60°, the mixture being well shaken. After a few minutes the silver chloride assumed a dense form, and crystallisation began. The silver chloride was then rapidly collected, and the filtrate, which no longer gave the reactions of the chloride ion, was allowed to crystallise. *Chromatopentamminecobaltic chromate* separated in glistening, scaly crystals, similar in colour to silver chromate. The yield was 1.5 grams. The crystals consisted of a trihydrate, which lost  $2\frac{3}{4}$  molecules of water after exposure over sulphuric acid in a vacuum for two or three weeks (loss = 7.16.  $2\frac{3}{4}\text{H}_2\text{O}$  require a loss of 7.17 per cent.). The resulting hydrate,  $4(\text{Co}_{5\text{NH}_3}^{\text{CrO}_4})\text{CrO}_4 \cdot \text{H}_2\text{O}$ , became anhydrous above 100°. The complete analysis of the trihydrate gave:

Found: Co = 17.48;  $\text{CrO}_3$  = 43.64;  $\text{NH}_3$  = 24.83;  $\text{H}_2\text{O}$  = 7.64.

$(\text{Co}_{5\text{NH}_3}^{\text{CrO}_4})\text{CrO}_4 \cdot 3\text{H}_2\text{O}$  requires Co = 17.09;  $\text{CrO}_3$  = 43.6;  $\text{NH}_3$  = 24.68;  $\text{H}_2\text{O}$  = 7.83 per cent.

*Tetrammine Series.*

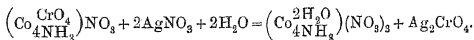
Carbonatotetramminecobaltic nitrate was prepared by Jörgensen's method (*Zeitsch. anorg. Chem.*, 1892, **2**, 282), and this was converted into diaquotetramminecobaltic nitrate by acidification of its solution. On treating the solution of diaquotetramminecobaltic nitrate with potassium chromate, either chromatotetramminecobaltic nitrate, chromatotetramminecobaltic chromate, or tri-chromato-octamminedicobalt could be obtained in the pure state, according to the conditions employed.

*Chromatotetramminecobaltic Nitrate*,  $2\left(\text{Co}_{4\text{NH}_3}^{\text{CrO}_4}\right)\text{NO}_3\cdot\text{H}_2\text{O}$ .—A solution of 4 grams of carbonatotetramminecobaltic nitrate in a little water was treated with dilute nitric acid, warmed gently to expel carbon dioxide, just neutralised with potassium hydroxide, and the volume made up to 40 c.c. Twenty grams of ammonium nitrate were dissolved in the liquid, and a solution of 1.2 grams of potassium chromate in 10 c.c. of water was added, drop by drop, in the cold, with vigorous stirring. The stirring was continued for a minute or two until crystallisation was complete, and the dark reddish-brown deposit was then immediately collected, washed with a little water, and dried in the air. The yield was 0.9 gram. The product was a hemihydrate, which lost its water of crystallisation after exposure for two days over sulphuric acid in a vacuum.

Found: Co = 18.86;  $\text{CrO}_3$  = 31.68;  $\text{NH}_3$  = 21.34;  $\text{H}_2\text{O}$  = 3.67.

$2\left(\text{Co}_{4\text{NH}_3}^{\text{CrO}_4}\right)\text{NO}_3\cdot\text{H}_2\text{O}$  requires Co = 18.77;  $\text{CrO}_3$  = 31.83;  $\text{NH}_3$  = 21.69  
 $\text{H}_2\text{O}$  = 2.87 per cent.

The salt was moderately soluble in water, giving a deep brown solution. Silver, barium, or lead salts did not precipitate the freshly prepared, cold solution, but precipitation took place at once on heating. The cold solution was also completely precipitated if allowed to remain for several days after the addition of the reagent, showing that the chromate radicle is gradually eliminated with the formation of a diaquotetrammine salt, for example,



*Chromatotetramminecobaltic Chromate*,  $\left(\text{Co}_{4\text{NH}_3}^{\text{CrO}_4}\right)\text{CrO}_4\cdot 3\text{H}_2\text{O}$ .—

Four grams of carbonatotetramminecobaltic nitrate in 80 c.c. of water were converted into diaquotetramminecobaltic nitrate as described above in the preparation of chromatotetramminecobaltic nitrate. To the cold neutral solution of diaquotetramminecobaltic

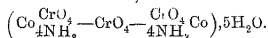
nitrate thus obtained (100 c.c.) 3 grams of potassium chromate, dissolved in 50 c.c. of water, were added with vigorous stirring. A brown, crystalline precipitate was formed, which was collected immediately, washed with water, and dried with alcohol and ether. The yield was 2.8 grams.

The salt contained three molecules of water as water of crystallisation only, being readily evolved when the substance was exposed in a vacuum over sulphuric acid. The salt was sparingly soluble in water, and its solution was immediately precipitated by silver nitrate, showing that some of the chromate content was ionisable. It follows from these facts and the analyses that the compound must have the formula assigned to it.

Found: Co=18.14; CrO<sub>3</sub>=45.31; NH<sub>3</sub>=20.61; H<sub>2</sub>O=8.26.

$(\text{Co}_4\text{CrO}_4)_2\text{CrO}_4 \cdot 3\text{H}_2\text{O}$ ; Co=17.97; CrO<sub>3</sub>=45.71; NH<sub>3</sub>=20.77;  
H<sub>2</sub>O=8.26 per cent.

*Trichromato-octamminedicobalt*,



—Two grams of carbonatotetramminecobaltic nitrate in 30 c.c. of water were converted into diaquotetramminecobaltic nitrate in the manner already described, and the cold neutral solution (50 c.c.) was added, with stirring, to a cold solution of 5 grams of potassium chromate in 50 c.c. of water. The clear liquid deposited a greenish-black, crystalline substance on keeping. This was collected, washed with a little water, and dried in the air.

Found: Co=17.14; CrO<sub>3</sub>=43.32; NH<sub>3</sub>=19.44; H<sub>2</sub>O=13.05.

Co<sub>2</sub>8NH<sub>3</sub>(CrO<sub>4</sub>)<sub>3</sub>·5H<sub>2</sub>O requires Co=17.04; CrO<sub>3</sub>=43.33;  
NH<sub>3</sub>=19.68; H<sub>2</sub>O=13.01 per cent.

The five molecules of water were readily evolved on exposing the compound in a vacuum over sulphuric acid, and all were therefore water of crystallisation only. In view of the facts ascertained with regard to chromatotetramminecobaltic chromate and described above, it follows that this isomeric compound must be a non-ionisable octamminedicobalt derivative. Its almost complete insolubility in water affords further confirmation of this view. Again, since in the diaquotetramminecobaltic salts the water molecules are in the "cis" position (Werner, "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 3rd ed., p. 347), this trichromato-octamminedicobalt must also have the chromate radicles in the "cis" position, and is therefore a 1:1':2'-trichromato-octamminedicobalt pentahydrate. Attempts to prepare the corresponding "trans" compound by various methods were unsuccessful.

*Chromatotetramminecobaltic Dichromate*,  $\left(\text{Co}_{4\text{NH}_3}^{\text{CrO}_4}\right)_2 \text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ .

—Four grams of carbonatotetramminecobaltic nitrate were converted into diaquotetramminecobaltic nitrate as described above, and the neutral solution (80 c.c.) was added slowly, with stirring, to a cold solution of 8 grams of potassium dichromate in 80 c.c. of water. The precipitate was immediately collected, washed with a little water, and dried in the air. The yield was 1.9 grams. Three separate preparations were analysed, and the ammonia content was low in every case, for some reason that could not be ascertained.

Found: Co = 15.94;  $\text{CrO}_3$  = 53.41, 54.01;  $\text{NH}_3$  = 17.48, 16.6, 16.4;  
 $\text{H}_2\text{O}$  = 4.98, 4.76, 5.04.

$\left(\text{Co}_{4\text{NH}_3}^{\text{CrO}_4}\right)_2 \text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  requires Co = 15.97;  $\text{CrO}_3$  = 54.19;  $\text{NH}_3$  = 18.4;  $\text{H}_2\text{O}$  = 4.88 per cent.

The three molecules of water were readily given off in a vacuum over sulphuric acid, and all were therefore water of crystallisation only. From the proportion of cobalt to chromium (2Co:4Cr) it is evident that the salt is chromatotetramminecobaltic dichromate,

$\left(\text{Co}_{4\text{NH}_3}^{\text{CrO}_4}\right)_2 \text{Cr}_2\text{O}_7$ , and not dichromatotetramminecobaltic chromate,

$\left(\text{Co}_{4\text{NH}_3}^{\text{Cr}_2\text{O}_7}\right)_2 \text{CrO}_4$ , in which the proportions are 2Co:5Cr. Consequently the dichromate radicle is ionisable, and the chromate radicle non-ionisable. The salt was moderately soluble in water, and the solution was immediately precipitated by silver and barium salts.

#### *Triamine Series.*

*Chromatohydroxotriaminocobalt.*—Two grams of trinitratotriaminocobalt prepared by Jørgensen's method (*Zeitsch. anorg. Chem.*, 1895, 5, 185) were dissolved in 40 c.c. of cold water, and the solution was added to a cold solution of 6 grams of potassium chromate in 40 c.c. of water. The brown precipitate (1) was collected, washed with cold water, and dried in the air, when it weighed 1.7 grams. The filtrate, on spontaneous evaporation, deposited crystals of potassium dichromate, as well as of potassium chromate. Two other preparations were made (2 and 3), in which 1 gram of potassium chromate in 10 c.c. of water was mixed with 6.25 c.c. of potassium hydroxide solution (1 c.c. = 0.0448 gram KOH), and the mixture was poured into a solution of 1.5 grams of trinitratotriaminocobalt in 10 c.c. of cold water. The analyses gave:

Found: (1)  $\text{H}_2\text{O}=11.5$ ;  $\text{CrO}_3=36.3$ ;  $\text{Co}=22.9$ ;  $\text{NH}_3=15.1$ .

(2)  $\text{H}_2\text{O}=11.4$ ;  $\text{CrO}_3=34.5$ ;  $\text{Co}=22.5$ ;  $\text{NH}_3=16.8$ .

(3)  $\text{NH}_3=16.7$ .

$\left( \begin{smallmatrix} \text{OH} \\ \text{CoCrO}_4 \\ 3\text{NH}_3 \end{smallmatrix} \right)_2 \cdot 2\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}=12.9$ ;  $\text{CrO}_3=35.8$ ;  $\text{Co}=21.1$ ;  
 $\text{NH}_3=18.3$  per cent.

Although impure, the compound was clearly a hydrated chromato-hydroxotriamminecobalt.

*Chromatoaquotriamminecobaltic Dichromate.*—Two grams of trinitratotriamminecobalt in 10 c.c. of cold water were added to a solution of 3 grams of sodium dichromate in 10 c.c. of water, and the mixture was treated with a solution of 0.75 gram of anhydrous sodium chromate in 10 c.c. of water, in the cold. A copious brown precipitate was formed, which was allowed to settle, and then collected, washed with a little water, and dried with alcohol and ether. The product, which weighed 1.4 grams, was only sparingly soluble in cold water. In a vacuum over sulphuric acid, it lost 3 molecules of water after three days, and a further quarter molecule after eighteen days, the weight then remaining constant. The analysis agreed closely with the formula given below.

Found:  $3\text{H}_2\text{O}=7.22$ ;  $3\frac{1}{4}\text{H}_2\text{O}=8.16$ ;  $\text{Co}=16.06$ ;  $\text{CrO}_3=54.09$ ;

$\text{NH}_3=13.63$ .

$\left( \begin{smallmatrix} \text{H}_2\text{O} \\ \text{CoCrO}_4 \\ 3\text{NH}_3 \end{smallmatrix} \right)_2 \cdot \text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  requires  $3\text{H}_2\text{O}=7.30$ ;  $3\frac{1}{4}\text{H}_2\text{O}=7.91$ ;  $\text{Co}=15.93$ ;  $\text{CrO}_3=54.04$ ;  $\text{NH}_3=13.81$  per cent.

*Note on the Preparation of Carbonatopentamminecobaltic Nitrate.*

The following method of preparation was found to be more convenient and more economical than that described by Werner and Goslings (*Ber.*, 1903, **36**, 2380).

Twenty grams of cobalt carbonate were dissolved in the smallest possible quantity of dilute nitric acid and the clear solution (100 c.c.) was poured into a mixture of 250 c.c. of concentrated aqueous ammonia and 100 grams of powdered ammonium carbonate. Air was drawn through for two or three hours and the solution was then allowed to remain for twenty-four hours. The mixture was heated for twenty minutes in a porcelain dish on the water-bath with frequent addition of a small piece of ammonium carbonate. The brown colour of the liquid changed to deep red, and the mixture was allowed to remain until crystallisation was complete. After filtration and washing with a little water, the salt

was digested with cold water to remove any ammonium carbonate still present. The air-dried product weighed 21 grams. (Found, Co=20.54; NH<sub>3</sub>=29.63. (C<sub>6</sub><sup>5</sup>NH<sub>3</sub>CO<sub>3</sub>)NO<sub>3</sub>·H<sub>2</sub>O requires Co=20.76; NH<sub>3</sub>=29.95 per cent.) The water was not given off at 100°, or in a vacuum over sulphuric acid at the ordinary temperature.

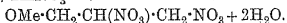
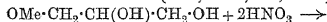
[Received, October 23rd, 1918.]

## VII.—*Glyceryl Methyl Ether Dinitrate (α-Methylin Dinitrate.)*

By DAVID TREVOR JONES.

DURING recent years, considerable attention has been devoted to the study of the mono- and di-nitrates of glycerol and their chlorides and ethers. The interest in these substances has been stimulated by the technical possibilities which they appeared to offer as ingredients of non-freezing nitroglycerin blasting compositions. Among the substances investigated have been the dinitrate of monochlorohydrin (Kast, *Zeitsch. ges. Schiess- u. Sprengstoffw.*, 1906, 1, 227), which has been more or less extensively used in such explosives as gelatin astralit, gelatin westfalit, etc. The mono- and di-nitrates of glycerol have been very exhaustively studied by Will (*Ber.*, 1908, 41, 1107), who commenced the investigation of these substances with the above-mentioned technical object in view. The dimethyl and diethyl ethers of glycerol mononitrate have been described by Paternò and Benelli (*Gazzetta*, 1909, 39, ii, 312), whilst Vender has described the dinitrates of monoacetin and monoformin (*Zeitsch. ges. Schiess- u. Sprengstoffw.*, 1907, 2, 21).

Glyceryl methyl ether dinitrate, which is here described, was prepared by the direct nitration of the α-monomethyl ether of Grün and Bockisch (*Ber.*, 1908, 41, 3471).



The product, which was readily isolated, was found to solidify after being well supercooled and stirred. It is a powerful explosive, having about two-thirds the strength of nitroglycerin. It is, however, much less sensitive to shock, although rather more readily exploded by heat. Its effect in lowering the freezing point of nitroglycerin is much the same as that of molecular concentra-

tions of monochlorohydrin dinitrate (Kast, *loc. cit.*) and of ethyl nitrate (Nauckhoff, *Zeitsch. angew. Chem.*, 1905, **18**, 21). All these values, however, are in complete disagreement with the value for the freezing-point constant of nitroglycerin as calculated from a carefully conducted determination of its latent heat of fusion (Hibbert and Fuller, *J. Amer. Chem. Soc.*, 1913, **35**, 979).

The substance did not appear to exist in a second or labile form corresponding with the labile form of nitroglycerin.

#### EXPERIMENTAL.

Glyceryl α-monomethyl ether was prepared by Grün and Bockisch's method (*loc. cit.*). The product distilled at 120°/18 mm., and the yield was 127 grams, or from 200 grams of monochlorohydrin 66 per cent. of the theoretical. The same yield was obtained on repeating the experiment.

#### *Glyceryl Methyl Ether Dinitrate.*

Sixty-three grams of glyceryl α-monomethyl ether were gradually added to 480 grams of a mixture of nitric and sulphuric acids ( $\text{HNO}_3 = 38.6$ ,  $\text{H}_2\text{SO}_4 = 59.0$ ,  $\text{H}_2\text{O} = 2.4$  per cent.), which was cooled in ice-water during the nitration. The initial temperature was 13°. During the operation, the temperature was allowed to rise to 20°, and was maintained at that point until the end. The nitration proceeded quite smoothly, and was easily controlled by regulating the addition of the glyceryl methyl ether. The time occupied by the nitration was from twenty to twenty-five minutes. The product was completely soluble in the mixed acid, and the mixture was slowly poured into 800 c.c. of water, the temperature being allowed to rise to 40°. The bulk of the dinitrate separated, and, after remaining for some little time, the bulk of the aqueous layer was poured off and preserved for extraction. The residue containing the dinitrate was neutralised with a semi-saturated solution of sodium carbonate. The dinitrate was then run off from below, the neutralised aqueous layer being added to the diluted acid which had been previously poured off. The dinitrate was then washed three times at 50° with an equal bulk of 5 per cent. sodium carbonate solution, then three times with water, and was finally dried in a desiccator over calcium chloride. The yield was 75 grams, or 64 per cent. of the theoretical. The neutralised aqueous washings were extracted with ether, and the ethereal solution was washed with 5 per cent. sodium carbonate solution, dried with calcium chloride, filtered, evaporated under diminished

pressure, and preserved over calcium chloride in a desiccator. In this way, a further yield of 13.9 grams was obtained, the total yield being thus 88.9 grams, or 77 per cent. of the theoretical.

The dry liquid constituting the first and major portion of the yield was analysed by the combustion method, but on account of its highly explosive nature the weighed-out substance was first converted into a weak dynamite by mixing with excess of previously ignited kieselguhr, the dynamite in turn being mixed with roughly powdered copper oxide and introduced into the combustion tube. The combustion proceeded normally.

The nitrogen was estimated by the nitrometer method, using sulphuric acid, as in the analysis of guncotton:

0.1397 gave 0.1248  $\text{CO}_2$  and 0.0514  $\text{H}_2\text{O}$ .  $\text{C}=24.36$ ;  $\text{H}=4.03$ .

0.5492 ,, 132.3 c.c.  $\text{NO}$  at  $16^\circ$  and 755 mm.  $\text{N}=14.15$ .

0.638 in 20.45 benzene gave  $\Delta^t = -0.833^\circ$ .  $\text{M.W.}=188$ .

$\text{C}_4\text{H}_8\text{O}_7\text{N}_2$  requires  $\text{C}=24.28$ ;  $\text{H}=4.08$ ;  $\text{N}=14.29$  per cent.

$\text{M.W.}=196$ .

The substance was therefore undoubtedly  $\alpha$ -methylin dinitrate.

*Glyceryl methyl ether dinitrate* crystallises in white, monoclinic prisms melting at  $24^\circ$ . As first obtained, it was a clear, colourless liquid, which became pale yellow on keeping. It crystallised with difficulty, and remained liquid, even with occasional shaking, for more than two years in a magazine maintained at  $15$ – $21^\circ$ . It distilled at  $124^\circ/18$  mm., that is, at approximately the same temperature as the glyceryl methyl ether from which it was derived, and some  $22^\circ$  lower than glyceryl dinitrate, the corresponding alcohol.

It is therefore more volatile than nitroglycerin, and when tested at  $100^\circ$  on a watch-glass it was found to volatilise at from seven to eight times as rapidly. The liquid has  $D_{20}^{15} 1.374$  and  $n_D^{20} 1.4478$ . It is soluble in benzene, toluene, acetic acid, methyl and ethyl alcohols, chloroform, ether, or acetone, and insoluble in carbon disulphide or light petroleum.

It gelatinises nitro-cotton rapidly at the ordinary temperature, and after warming it yields a gelatin softer and more plastic than that obtained from nitroglycerin.

The chief interest of this substance lies in its explosive properties as compared with those of nitroglycerin. It has about two-thirds the power of nitroglycerin, although it is much less sensitive to shock. Its comparative insensitiveness was demonstrated by submitting to the fall-hammer test unfrozen dynamites each containing three parts of explosive to one part of kieselguhr. Both substances were placed under a steel disk and subjected to the



impact of a weight of 1 kilogram, falling from a measured height. The results are set forth in the following table:

Dinitrate.			Nitroglycerin.		
Height of fall. cm.	Detonations.	Failures.	Height of fall. cm.	Detonations.	Failures.
100	2	8	30	10	0
95	1	9	20	10	0
90	1	9	15	9	1
85	0	10	10	0	10

The solid substance was very insensitive. It did not explode even when scratched with the sharp edge of a thin melting-point tube. On the other hand, the dinitrate proved to be more easily exploded when heated than did nitroglycerin. When heated in a glass test-tube in a metal-bath, the temperature being raised at the rate of 5° per minute, it was observed to explode at 182°, the trinitrate exploding at 192°.

Comparative power tests of nitroglycerin and methylin dinitrate dynamites were made with the Trauzl lead block and mortar tests. In the lead block, the dinitrate dynamite gave an expansion of 22.9 c.c., a similar charge of nitroglycerin dynamite giving 30.0 c.c. In the mortar test, the relative powers indicated by the ballistic pendulum were 93.76 kilogram-metres (678 foot-lb.) for the dinitrate dynamite as compared with 124.43 kilogram-metres (900 foot-lb.) for a similar charge of nitroglycerin dynamite. Methylin dinitrate, therefore, would appear to have rather more than two-thirds the strength of nitroglycerin.

In order to determine the lowering effect of the dinitrate on the freezing point of nitroglycerin, a form of apparatus was adopted similar to that used by Kast (*loc. cit.*) for determining the melting points of the nitroglycerin isomerides, and by Hibbert (*Eighth International Congress of Applied Chemistry*, 1912, IV, 37).

About 5 c.c. of the mixture were inserted in a test-tube (15 × 1 cm.) which was fitted into a slightly larger tube, whereby the glyceryl nitrates were protected by an air-jacket from the too rapid action of the freezing mixture. The freezing agent consisted of ice where mixtures of higher melting point were concerned, and of ice and salt for those of lower melting point. The thermometer was allowed to stand in the mixture, direct contact between glass and glass being prevented by enclosing the lower portion of the thermometer bulb in a band of elastic. The stirrer consisted of a flexible piece of platinum wire which was attached to a weighted string wound over a simple pulley, and fastened at

the further end to the outer edge of a wooden disk rotated by a motor. The liquid was first supercooled to the extent of about  $4^{\circ}$  or  $5^{\circ}$ . It was then inoculated with a small quantity of a frozen mixture of nitroglycerin, wood-pulp, and sodium nitrate, and vigorously stirred. The maximum temperature was then carefully noted and taken as the freezing point. It will be seen that the values found for the molecular depression constant for nitroglycerin vary from 72.4 to 81.0, thus differing not very greatly from those obtained by Nauckhoff (*loc. cit.*) and by Kast (*loc. cit.*) with ethyl nitrate and monochlorohydrin dinitrate respectively. These numbers are in fair agreement with the value 70.5 for the freezing-point constant for nitroglycerin obtained by Nauckhoff (*loc. cit.*) from a determination of its latent heat of fusion. Nauckhoff's method was, however, admittedly defective, and his results differ very considerably from those of Hibbert and Fuller (*loc. cit.*), who found the latent heat of fusion ( $h$ ) of nitroglycerin at  $0^{\circ}$  to be 33.2 calories. Corrected to  $13^{\circ}$ , the melting point of stable nitroglycerin, this would become  $33.2 + 13.0$  ( $c_1 - c_2$ ), where  $c_1$  and  $c_2$  are the specific heats of solid and liquid nitroglycerin respectively. Accepting Nauckhoff's values of 0.356 and 0.315 for these, the latent heat of fusion of nitroglycerin at  $13^{\circ}$  would be  $33.2 + 13.0$  ( $0.356 - 0.315$ ) = 34.33.

Hence the freezing-point constant

$$\frac{RT^2}{100h} = \frac{0.1991 \times (273 + 13)^2}{100 \times 34.33} = 48.5.$$

The results are set forth in the following table, which includes Nauckhoff's and Kast's values derived from ethyl nitrate and chlorohydrin dinitrate:

Composition of liquid.		Depression of freezing point. ( $\Delta$ )	Molecular depression constant.	
Nitro-glycerin. Grams.	Methylin dinitrate. Grams.		Calculated from $\Delta$	Calculated from latent heat (Hibbert and Fuller).
31.69	1.802	2.1°	72.4	48.5
15.31	1.748	4.4	75.6	"
8.22	1.729	8.7	81.0	"
Chloro-hydrin dinitrate.				
21	2.1	4.4	88.4	"
21	4.2	6.4-7.2	62.7-70.5	"
21	6.3	9.4	60.7	"
Ethyl nitrate.			74.1	
			76.0	

Attempts to obtain a labile form of the substance analogous to that of nitroglycerin were made. The liquid was mixed with glass wool and supercooled to varying degrees, with continual stirring with a glass rod. When some of the supercooled liquid which had not been previously frozen was inoculated with a trace of this product, the solid obtained invariably crystallised at  $24^{\circ}$ .

The author desires to express his indebtedness to Messrs. Nobel's Explosive Co. and to Mr. W. Rintoul, the manager of their Research Section, for the facilities accorded to him for the carrying out and publication of this work.

ARDEER.

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### VIII.—*The Inflammation of Mixtures of Ethane and Air in a Closed Vessel: The Effects of Turbulence.*

By RICHARD VERNON WHEELER.

WHEN describing the inflammation of mixtures of methane and air it was noted that the speed at which flame spreads through the mixture in a closed vessel is demonstrably dependent on the degree of mechanical agitation imparted to the mixture, as, indeed, is the speed of flame in all combustible mixtures and under all conditions other than those existing during the propagation of the explosion wave.

This important fact appears first to have been observed, or, at all events, first commented on by Schloësing and de Mondésir about the year 1864. Their experiments, which involved an extended study of the mode of propagation of flame, were carried out mainly with mixtures of carbon monoxide and air, and were undertaken in connexion with a research on the working of gas engines. Mallard and Le Chatelier, to whom the results of the experiments were communicated verbally, have thus described them (*Ann. des Mines*, 1883, [VIII], 4, 298):

“Ces recherches ont mis en évidence un fait d'une grande importance, l'influence de l'agitation du mélange gazeux sur la vitesse de propagation de la flamme. Des mélanges très lents (et par cette expression nous entendrons ceux dans lesquels la vitesse de propagation est faible) peuvent donner lieu à des propagations pour ainsi dire instantanées, c'est-à-dire à de véritables explosions, quand on provoque au moment de l'inflammation une agitation intérieure très

vive, telle que celle que l'on obtient en faisant déboucher au milieu d'une masse gazeuse en repos un jet de gaz animé d'une grande vitesse."

These observations appear to have been overlooked or forgotten until the subject of the agitation or turbulence of gaseous mixtures became of manifest importance during the investigation of gaseous explosions instituted by the British Association for the Advancement of Science. New experiments on the subject, by Dugald Clerk and Hopkinson, are recorded in the Fifth Report of the Committee on Gaseous Explosions (*Rep. Brit. Assoc.*, 1912, 201).

To quote from his Gustave Canet lecture (Junior Institution of Engineers, 1913), Dugald Clerk "had long ago observed that gas engines would have been impracticable had the rates of explosion been the same in actual engine cylinders as in closed-vessel experiments." During his experiments in 1912 he "found that the rate of explosion rise in the same engine varied with the rate of revolution, increasing with increased number of rotations per minute, and was due to the turbulence or eddying caused by the rush of gases into the cylinder during the suction stroke, which persisted during the compression stroke."

By drawing in a charge of mixture into the gas-engine cylinder in the ordinary way, and then tripping the valves and compressing and expanding the charge for one or two revolutions before igniting it, the turbulence was given time to die away. It was found that the effect of thus damping down turbulence was to retard the rate of inflammation of the mixture to a remarkable extent. For example, with a mixture of coal-gas and air containing about 9.7 per cent. of gas, ignition in a gas-engine cylinder under normal conditions at the end of the first compression stroke (the engine being run at 180 revolutions per minute) resulted in the maximum pressure being attained after 0.037 sec.; whilst when ignition was at the end of the third compression stroke, after the charge had been expanded twice and turbulence had subsided, the time taken for the attainment of maximum pressure was 0.092 sec.

Hopkinson experimented on the effects of turbulence at the same time as Dugald Clerk, using a cylindrical vessel 30.5 cm. in diameter and 30.5 cm. long. A small fan was mounted at the centre of the vessel, and comparison was made of the results of igniting similar mixtures with the fan at rest and in motion. With mixtures of coal-gas and air containing 10 per cent. of gas, the times that elapsed between ignition and the attainment of maximum pressure were: (1) with the fan at rest, 0.13 sec.; (2) with the fan running at 2,000 revolutions per min., 0.03 sec.; and (3) with the fan running at 4,500 revolutions per min., 0.02 sec.

Simultaneously with, and independently of, the experiments thus made on behalf of the Gaseous Explosions Committee of the British Association, a problem under investigation for the Explosions in Mines Committee of the Home Office was found to involve a study of the effects of turbulence on the inflammation of gaseous mixtures. The problem was to determine the effect, if any, of the presence of incombustible dusts in suspension on the limits of inflammability of mixtures of firedamp and air. A series of experiments on the ignition of mixtures near the lower limit of inflammability was made with a spherical vessel of about 4 litres capacity (described in T., 1918, **113**, 855) provided with a fan which could be rotated at a high speed so as to agitate the mixture and maintain dust in suspension. Naturally, the fan was rotated whether dust was present or absent, so as to ensure that the comparative experiments required should be made under as far as possible identical conditions. The pronounced effect of turbulence or agitation of a gaseous mixture on the speed at which flame travels through it thus became manifest, for many experiments had previously been made with similar mixtures in the same sphere without the fan.

The fan had four blades, and was attached to a horizontal shaft passing through an air-tight gland near the bottom of the sphere. Each blade extended for 7.5 cm. along the shaft and had a maximum width of 2.5 cm., the edge having a radius of curvature of 9.5 cm. The shaft was so fitted that there was a clearance of 1 cm. between the side of the sphere and the edges of the fan-blades. A slight helical twist was given to each blade.

Several experiments were made with mixtures of ethane and air near the lower-limit of inflammability, which, with ignition at the centre of a closed spherical vessel of glass of 2.5 litres capacity, is 3.10 per cent. ethane. With 3.0 per cent. of ethane flame travels slowly throughout nearly the whole of the (non-turbulent) mixture in such a vessel; and with 2.9 and 2.95 per cent. of ethane flame spreads through about one-third of the mixture (T., 1911, **99**, 2026). It will therefore be realised that even though a mixture may not contain sufficient ethane to ensure continued self-propagation of flame, part of the mixture may be burnt with a consequent development of pressure in a closed vessel.

The earlier experiments with turbulent mixtures were made with the fan running at 100 revolutions per second. The means of ignition was a secondary discharge (from a "10-inch" X-ray coil) across a spark-gap of 12 mm. at the centre of the sphere, produced by breaking a current of 10 amperes in the primary circuit of the coil, the trembler being locked. Such a discharge is more than adequate to ignite any inflammable mixture of ethane and air when

the mixture is still, yet it was found that no ignition, or, rather, no propagation of flame, took place with a mixture of ethane and air containing as much as 3.2 per cent. of ethane when that mixture was agitated by the fan at 100 revolutions per second. On stopping the fan and allowing the turbulence to subside, ignition took place readily with complete inflammation of the mixture and the development of a pressure of 3.4 atmospheres.

Similarly, with mixtures containing 3.15 and 3.05 per cent. of ethane no ignition could be obtained, whilst the fan was running (at 100 revolutions per second), however frequently the discharge was passed, although when the mixtures were free from turbulence ignition occurred on the first passage of the discharge. Details of these and similar experiments are as follow:

Ethane in mixture. Per cent.	Result.
3.20	No ignition when the fan was running at 100 revolutions per sec. With the fan at 40 revolutions per sec. ignition took place, a pressure of 4.5 atm. being recorded 0.25 sec. after ignition. Without the fan running, a pressure of 3.4 atm. was developed.
3.15	No ignition could be obtained when the fan was running at 100 revolutions per sec. Without the fan, ignition occurred at once, a pressure of 3.2 atm. being recorded.
3.10	With the fan at 40 revolutions per sec. ignition occurred on the fourth passage of the discharge. With the fan at 20 revolutions per sec. ignition occurred at once. A pressure of 4.4 atm. was developed on both occasions, 0.177 sec. after ignition in the first experiment, and 0.287 sec. after ignition in the second.
3.05	No ignition could be obtained when the fan was running at 100 revolutions per sec. Without the fan, ignition occurred at once and a pressure of 2.8 atm. was recorded.
3.00	No ignition with the fan at 100 revolutions per sec. With 20 revolutions per sec. ignition occurred at once and a pressure of 4.3 atm. was recorded 0.30 sec. after ignition.
2.95	With the fan running at 20 revolutions per sec. ignition occurred when the discharge was maintained (the trembler of the coil being in action). A pressure of 4.2 atm. was recorded.

Strong agitation of a mixture poor in combustible gas renders it difficult to ignite, or, to be precise, renders it difficult for the flame that no doubt occurs during the passage of the discharge to spread away therefrom and travel throughout the mixture. This difficulty increases as the degree of agitation is increased and as the percentage of combustible gas is decreased. When, however, the flame in such an agitated mixture does manage to spread away from the source of ignition it travels rapidly.

From the high pressure developed when a mixture was ignited that contained 2.95 per cent. of ethane and to which turbulence

had been imparted by a fan running at 20 revolutions per second, it seemed that flame must have travelled through a greater proportion of the mixture than the one-third observed when the mixture was quiescent. An apparatus was therefore devised to enable the appearance of the flames in turbulent mixtures to be examined. The apparatus, which consisted essentially of a globe of glass of about 4 litres capacity, is shown in Fig. 1, and needs no description. Preliminary experiments were made to determine the direction of the air-currents induced by the fan, which had two helical blades and revolved on a vertical axis. From the behaviour of coloured powders introduced into the globe while the fan was spinning it appeared that air was drawn from the centre of the globe towards the axis of the fan, and was discharged at the periphery of the latter as a spiral current directed obliquely\* around the walls of the globe.

Mixtures of methane and air were used for the experiments. Normally, the lower-limit for central ignition of methane-air mixtures in a closed sphere is 5.6 per cent. methane; the flame travels upward from the spark at the centre until it occupies one-third of the vessel, when it travels downwards as a horizontal disk to the bottom. The appearance of the flames in mixtures containing less than 5.6 per cent. of methane is shown in Fig. 3, T., 1911, 99, 2025.

When a 5.6 per cent. mixture of methane and air was agitated by spinning the fan at about 50 revolutions per second, a succession of discharges from an induction coil, the trembler of which was in operation in the usual manner, apparently failed to cause ignition. On close observation, however, it was seen that a pointed tongue of flame appeared at each passage of the discharge directed *downwards* towards the axis of the fan, apparently drawn thither by the current. The flame was about 2 cm. long and formed a sharp-pointed cone having the spark-gap (12 mm. in length) as its base. Occasionally, if the discharge were maintained, a fine filament of flame darted rapidly over a distance of a few cm. towards the fan. The speed of the fan was now reduced to about 30 revolutions per second and a discharge passed across the gap. The sequence of events was too rapid to be followed by the eye. It was observed that a downward-pointing tongue of flame was produced as before, and that this tongue, after some hesitation, shot towards the axis of the fan; the whole vessel then seemed to fill with flame and the glass was shattered into powder.

Further experiments were made with mixtures containing less methane. On two occasions the globe was shattered owing to the

\* No doubt owing to an unequal setting of the blades of the fan.

rapidity with which the mixture contained in it was inflamed, but in a number of experiments, notably in several with a mixture containing 5.0 per cent. of methane (see T., 1914, 105, 2595), the movement of the flame could be followed; or, at all events, owing to the persistence of retinal impressions, the course taken by the flame was apparent. An attempt has been made to indicate the appearance of the flame to the eye at a given instant by the shaded additions to Fig. 1. The impression produced can be described as that of a spiral whirlwind of flame, the axis of the spiral being inclined at an angle; in effect, the flame seemed to follow the course of the current induced by the fan. It appeared also that the flame passed several times through the mixture before it finally died away at the centre of the sphere. Analysis of the products of combustion of the 5.0 per cent. mixtures of methane and air showed that all the methane had been burnt.

There can be little question, as a result of these observations, that the action of the form of turbulence studied in causing an enhanced speed of combustion of a weak inflammable mixture of methane or ethane and air within a closed vessel is purely mechanical. The flame, which normally would be propagated mainly by conduction of heat from a burning to an unburnt "layer" of mixture, is forcibly dragged in the wake of the rapid current induced by the fan, burning the mixture in its path. The difficulty experienced by the flame in such weak mixtures in travelling away from the source of ignition if the speed of the fan is very great is no doubt due to the fact that mixtures of the paraffins with air exhibit a considerable "time-lag" when the temperature of the source of heat that causes ignition is but little above the ignition-temperature, a condition obtaining with the flames of limit mixtures.

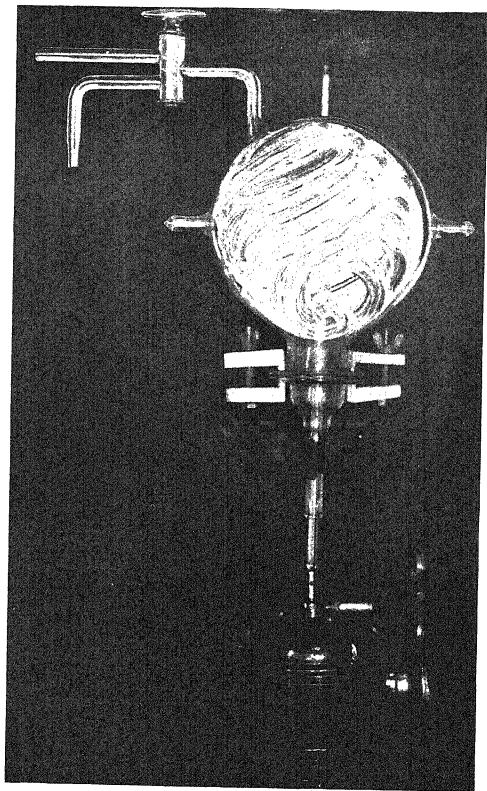
With richer mixtures, in which flame normally spreads at an equal speed in all directions from the source of ignition, the action of turbulence is mechanical also. To quote Mallard and Le Châtelier (*loc. cit.*, p. 350):

"Lorsque le gaz dans lequel progresse la flamme est à l'état d'agitation, la vitesse de propagation augmente parceque la chaleur se transmet non seulement en vertu de la conductibilité du mélange gazeux, mais encore en vertu des différences de vitesse des diverses parties de la masse. La surface de la flamme, au lieu de garder une forme constante et régulière, se déforme à chaque instant, augmente de largeur en multipliant les points d'inflammation et, par suite, en rendant plus rapide la progression de la combustion."

If this explanation is correct, it follows that (1) the greater the turbulence the more rapid should be the combustion; and (2) a



FIG. 1

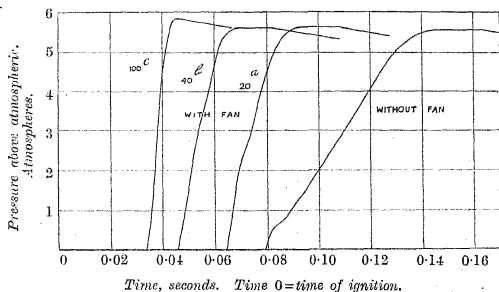




mixture in which the speed of flame normally is slow should be more susceptible to the effects of turbulence than one in which the speed of flame normally is rapid.

The first deduction has received experimental verification by Hopkinson, whose results have already been quoted. His results are confirmed by a series of experiments in the 4-litre sphere with mixtures of ethane and air containing 3.85 per cent. of ethane, the time-pressure curves for which are reproduced in Fig. 2. The time-intervals between ignition and the attainment of maximum pressure were: mixture at rest, 0.146 sec.; fan running at (a) 20 revs. per sec., 0.091; (b) 40 revs. per sec., 0.070 sec.; (c) 100 revs. per sec., 0.045 sec. Additional points that should be

FIG. 2.



noted as regards these curves are: (1) the slight increase of pressure obtained with the turbulent mixtures (a) and (b), and the marked increase with the turbulent mixture (c) as compared with that produced by the quiescent mixture; and (2) the disappearance from the curve for turbulent mixture (c) of the horizontal portion at maximum pressure noticeable in the other three curves. An explanation of these effects is offered later.

In order to test the second deduction that should follow if the explanation suggested for the action of turbulence is correct, two series of experiments were made with mixtures of ethane and air ranging between the lower-limit mixture and that giving the maximum pressure on combustion. In the one series the fan was run at a constant speed of 100 revolutions per second; in the other the

fan was at rest. The time-pressure curves for typical experiments of these two series are shown in Figs. 3 and 4,\* the curves for the

FIG. 3.

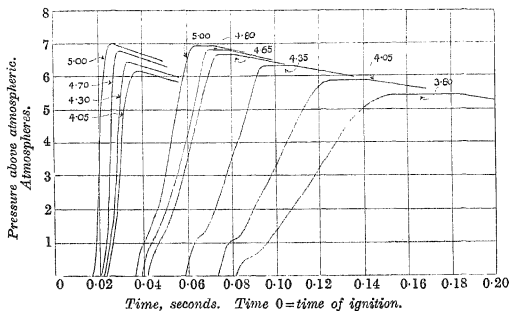
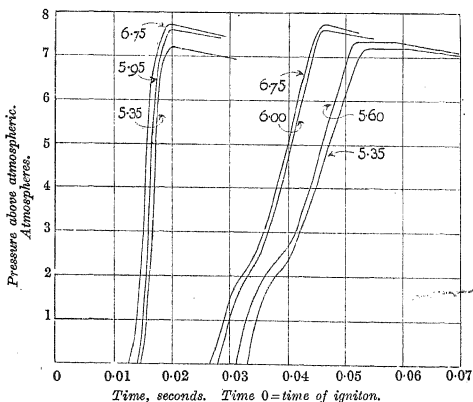


FIG. 4.



\* It should be noted that the unit of time employed in plotting the curves in Fig. 3 (and Fig. 2) is double that in Fig. 4. This contraction of the time-scale is rendered necessary from considerations of space.

turbulent mixtures occupying the left-hand portion of each diagram.

From these curves the time that elapsed between ignition and the attainment of maximum pressure for each mixture can be determined. These times, together with the times for mixtures not included in Figs. 3 and 4, are recorded in the table that follows:

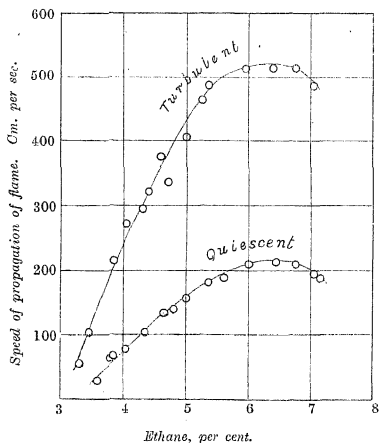
Ethane in mixture. Per cent.	Time between ignition and the attainment of maximum pressure. Seconds.	
	Without turbulence.	With turbulence.
3.30	—	0.176
3.45	—	0.096
3.60	0.332	—
3.80	0.152	—
3.85	0.146	0.045
4.05	0.124	0.036
4.30	—	0.033
4.35	0.094	—
4.60	—	0.026
4.65	0.073	—
4.70	—	0.029
4.80	0.070	—
5.00	0.063	0.024
5.25	—	0.021
5.35	0.054	0.020
5.60	0.052	—
5.95	—	0.019
6.00	0.0465	—
6.40	—	0.019
6.45	0.046	—
6.75	0.0465	0.019
7.05	0.050	0.020
7.15	0.052	—

It has been shown (T., 1918, 113, 852) that these time-intervals can be used to calculate, for each mixture, the mean speed of propagation of flame between the centre and the top of the sphere, a distance of 9.75 cm. The speeds thus calculated are shown plotted against percentages of ethane in Fig. 5. Allowing for the irregularities, which are naturally more noticeable with the turbulent than with the quiescent mixtures, the speeds for equivalent percentages of ethane in the two sets of experiments, as deduced from the smoothed curves, are given in the table on p. 90.

The conclusion that a mixture in which normally the speed of flame is slow should be affected by turbulence to a greater extent than one in which normally the speed of flame is rapid is thus proved experimentally by the gradual diminution in the value of the ratio  $B/A$ .

*The Development of Pressure.*—On referring to the time-pressure curves for mixtures without turbulence given in Figs. 3 and 4, and

FIG. 5.



comparing them with the curves for mixtures of methane and air previously published (*loc. cit.*, Fig. 2, p. 847), it will be seen that

*Mean Speed of Propagation of Flame from Centre to Top of Sphere. Cm. per sec.*

Ethane in mixture. Per cent.	Without turbulence. (A).	With turbulence. (B).	Ratio B/A.
3.6	35	142	4.06
3.8	55	195	3.54
4.0	75	237	3.17
4.2	95	284	2.99
4.4	112	320	2.85
4.6	129	360	2.79
4.8	144	400	2.77
5.0	158	430	2.72
5.2	172	462	2.68
5.4	185	485	2.62
5.6	195	500	2.56
5.8	202	510	2.52
6.0	210	518	2.47
6.5	212	518	2.44
6.7	200	495	2.47

both sets of curves are of the same type. All the mixtures of

ethane and air up to and including that containing 5.6 per cent. of ethane have time-pressure curves which exhibit the three stages of development noticeable with the mixtures of methane and air. The explanation of these stages offered when describing the methane curves can be applied also in the present instance.

Support is given to the assumption then made that the second stage of development, during which the recorded pressure remains constant, represents a balance between a gradual decrease of pressure that begins as soon as inflammation of the mixture is complete and is due to cooling by the walls of the vessel, and an increase of pressure incident at the same moment and due to the gradual attainment of thermal equilibrium. For it will be found that a graphical "correction" applied, in conformity with this assumption, in the manner described (*loc. cit.*, p. 849) yields results for the maximum pressures in close agreement with the maxima recorded by equivalent mixtures when turbulent, over the whole range from 3.80 per cent. ethane (at and above which percentage the flame travels from the centre in all directions at the same speed) upwards.

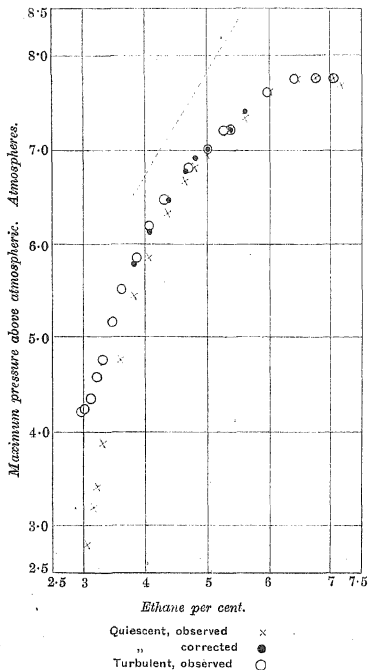
This is best shown in Fig. 6, where the observed maximum pressures for all the mixtures experimented with, both turbulent and quiescent, and the "corrected" maxima for the latter, are shown plotted against percentages of ethane. It should be observed that the magnitude of the correction, as is to be expected, diminishes in proportion as the speed of inflammation of the mixture increases. Similarly, the magnitude of the difference between the maximum pressures recorded with like mixtures when turbulent and quiescent also decreases as the speed of inflammation of the latter increases, until with mixtures containing more than 5.6 per cent. of ethane no difference is observable between the two sets of pressures. Further, the crests of the time-pressure curves for the quiescent mixtures that contain more than 5.6 per cent. of ethane no longer remain horizontal over a measurable length of time, but the cooling curves begin as soon as the maxima are attained.

Pier (*Zeitsch. Elektrochem.*, 1909, 15, 536), who used the pressures developed by the inflammation of different mixtures in a closed vessel to determine the specific heats of various gases, has made observations which have a bearing on the question of the effects of turbulence.

Using a manometer of similar construction to the Petavel gauge (*Phil. Mag.*, 1902, [vi], 3, 461), Pier found exact agreement between the observed and the calculated pressures produced by mixtures the combustion-temperatures of which exceeded 1600°. For this reason he combatted Nagel's opinion ("Versuche über Zundgeschwindig-

heit explosibler Gasmische," *Mitteilungen über Forschungsarbeiten des Ingenieurwesens*, Vol. 54, 1908) that with central ignition in a spherical vessel the mixture near the walls must be raised in temperature by adiabatic compression before flame reaches it

FIG. 6.



(an opinion that had already received experimental verification by Hopkinson), and suggested that the interchange of heat between different portions of the mixture within the vessel must be practically instantaneous.



This result Pier supposed would be effected by a rapid whirling and mixing of the contents of a spherical vessel owing to a sudden increase of pressure on ignition at the centre. It is clear, if only by reason of the difference observable in the character of the time-pressure curves for ethane-air mixtures with and without artificially-produced turbulence, that Pier's contention cannot be correct; and Hopkinson's measurements of the temperatures within a closed cylindrical vessel at the moment of maximum pressure produced by the inflammation of a mixture of coal-gas and air (*Proc. Roy. Soc.*, 1906, [A], 77, 387) should have convinced Pier of its falsity.

In the absence of knowledge regarding the composition of the products of combustion at the moment of attainment of maximum pressure when the ethane-air mixtures contain excess of ethane, it is not possible to calculate the theoretical pressures that should be given by such mixtures on ignition in a closed sphere were there no loss of heat during the propagation of flame. Calculation can, however, be made for those mixtures in which the combustion of ethane can be presumed to be complete. The mixture of ethane with air in which ethane and oxygen are in the theoretical proportions for complete combustion to form carbon dioxide and steam contains 5.63 per cent. of ethane. The dotted line in Fig. 6 represents the calculated maximum pressures over the range 3.8—5.5 per cent. ethane.\* It will be seen that a loss of heat of between 9 and 12 per cent., presumably due to radiation during the propagation of flame, is indicated.

A matter for further study is the fact that the mixtures of ethane and air which produce the highest pressures are not those within close range of the mixture containing ethane and oxygen in theoretical proportions for complete combustion (5.63 per cent. of ethane), but lie over a considerably higher range, namely, 6.5—7.0 per cent. The time taken for the attainment of maximum pressure reaches a minimum over the same range, or, in other words, the speed of propagation of flame under the conditions of the experiments is fastest in mixtures containing between 6.5 and 7.0 per cent. of ethane. In this respect the results obtained with mixtures of ethane and air differ markedly from those with methane and air.

Further comparison of these results with those obtained with mixtures of methane and air is reserved for a future communication, which will include the results of similar experiments with other members of the paraffin series of hydrocarbons.

\* The calculations were made in the manner described in T., 1918, 113, 858, using Langen's values for the specific heats of the gases.

## EXPERIMENTAL.

The apparatus used (4-litre sphere) and general method of procedure for the experiments has already been described (*loc. cit.*, p. 854). The ethane was prepared by the action of water on zinc ethyl and was purified by liquefaction by liquid air; the ratio  $O/A$  on explosion analysis was 1.25, showing that it contained no impurity.

The majority of the experiments described in this paper were carried out during the year 1912, with the assistance of Mr. M. J. Burgess.

[Received, November 15th, 1918.]

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## IX.—*The Ignition of Explosive Gases by Electric Sparks.\**

By JOHN DAVID MORGAN.

SOME time ago an investigation was carried out by Dr. R. V. Wheeler and Prof. W. M. Thornton on the ignition of explosive gases by sparks produced in signal bell circuits (Home Office Report on Electric Signalling with Bare Wires, R. V. Wheeler and W. M. Thornton, June, 1916). They used iron-core coils, in conjunction with mechanical means for breaking the circuit. Commenting on the results obtained, they state:

"It may be said that ignition by a rapid break flash at a low circuit voltage depends on the inductance voltage at which the flash is formed, and the igniting power of the flash is proportional to the product  $Li$  (where  $L$  is the inductance of the circuit and  $i$  the current prior to breaking the circuit). When the break of the circuit is made slowly, the igniting power of the flash has been found to depend upon its energy,  $\frac{1}{2}Li^2$ . There are thus two limiting conditions for the igniting power of the flash; at the one the inductance voltage is of importance, at the other the energy. For any given gaseous mixture there is a range of rapidity of break over which the two types of ignition blend, so that under certain conditions the igniting power of the flash may be proportional

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neither directly to  $i$  nor to  $i^2$ , but to some intermediate value of it."

Then, referring to a previous report (Home Office Report on Battery Bell Signalling Systems, R. V. Wheeler, January, 1915), they cite a case in which it was found that the igniting power of the break flash could be expressed by the relationship  $Li^{1.4}$  = constant.

The figures by Wheeler and Thornton in support of the conclusion that  $Li$  is constant are given in table I.

TABLE I.

Inductance ( $L$ ). Henries.	Igniting current ( $i$ ) at 25 volts. Ampere.	$Li$ .
0.27	0.82	0.220
0.47	0.45	0.212
0.70	0.26	0.182
0.90	0.20	0.180
1.04	0.17	0.177
1.18	0.155	0.183
1.27	0.145	0.184
1.31	0.13	0.170
1.60	0.11	0.176
2.00	0.09	0.180

In the same report they give the number of layers of wire on the magnets used by them, together with the igniting currents. These are given in table II. I have added a third column giving the product  $N^2i^2$ , where  $N$  = number of layers. As the layers each have the same number of convolutions,  $N$  is proportional to the turns. It will be noticed that it can also be said that  $N^2i^2$  is constant, a quantity which has not the same physical significance as  $Li$ . The expressions are only comparable when each contains either of the terms  $i$  or  $i^2$ .

TABLE II.

Layers of wire on magnet ( $N$ ).	Igniting current ( $i$ ).	$N^2i^2$ .
4	0.82	10.8
8	0.45	12.8
12	0.26	9.7
16	0.20	10.0
18	0.17	9.3
20	0.155	9.6
22	0.145	10.0
24	0.13	9.7
28	0.11	9.6
32	0.09	8.4

In the earlier report by Dr. Wheeler, a table is given from which the number of layers on the magnet coil can be deduced, and

the igniting current is added. Using these figures, I have calculated  $N^2i^2$ , and the figures are given in table III.

TABLE III.

Number of layers ( <i>N</i> ).	Igniting current ( <i>i</i> ).	$N^2i^2$ .
20	0.17	11.6
16	0.23	13.6
12	0.33	15.6
8	0.55	19.2
6	0.95	32.5

The figures in the third column show that in this case the product  $N^2i^2$  is by no means constant, but progressively increases.

When the flux produced by the current is linked with the whole of the windings, the product  $N^2i^2$  is proportional to the electrokinetic energy of the system so long as the permeability is constant. When the linkage is imperfect or the permeability varies, the energy is not proportional to  $N^2i^2$ . From the results above referred to, it is found that when a low tension igniting spark is defined in terms of the coil constants (*N* or *L*) and the current (*i*) prior to the spark, the energy required to produce a spark that will ignite a gas mixture of given composition appears to be constant in some cases and not constant in others.

Experiments with low tension sparks have led me to suspect that such results as those above mentioned, though apparently diverse, have some constant factor in common, and that the disparities are due to the manner in which the results are expressed. There is not implied by this remark any suspicion of the accuracy of the work done by Wheeler and Thornton. They were concerned mainly with determining what circuit conditions could give rise to dangerous sparks, and from that point of view the results were expressed in terms of practical utility. The question raised is as to whether the results as expressed can be employed to determine the property of the spark on which ignition depends.

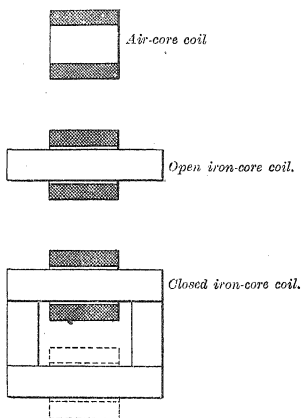
I therefore decided to make a new investigation with low tension sparks, and arrange the experiments to cover a wide range of different magnetic conditions. Six short air-core coils were made according to the particulars given in table IV.

TABLE IV.

No.	Number of turns.	Number of layers.
1	100	2
2	200	4
3	300	6
4	400	8
5	500	10
6	700	14

Two iron cores of relatively large cross-section were also made, one a laminated bar and the other a closed laminated frame, for use with the same coils. The experiments were divided into three groups, which were distinguished only by the differences in the magnetic conditions of the cores. Diagrammatic representations of the coils are shown in Fig. 1. Current was obtained from a 12-volt accumulator. The circuit was completed by a variable

FIG. 1.



resistance of negligible inductance, an ammeter, and a 'flick' contact breaker, the latter being enclosed in the explosion chamber. The contact breaker consisted of a flexible steel prong capable of being rotated into contact with a fixed steel stem, and then flicked over the stem. A coal gas and air mixture of constant composition was used throughout the investigation.

The least currents required to produce ignition are given in table V.

TABLE V.

*Air-core Coils.*

No. of layers ( $N$ ).	Current ( $i$ ) amperes.	$N^2i^2$ .
2	4.5	81
4	2.05	67.4
6	1.2	54
8	0.83	44
10	0.575	33
14	0.35	24

*Open Iron-core Coils.*

No. of layers ( $N$ ).	Current ( $i$ ) amperes.	$N^2i^2$ .
2	1.05	4.4
4	0.51	4.3
6	0.35	4.4
8	0.26	4.3
10	0.21	4.4
14	0.15	4.4

*Closed Iron-core Coils.*

No. of layers ( $N$ ).	Current ( $i$ ) ampere.	$N^2i^2$ .
2	0.63	1.6
4	0.32	1.64
6	0.2	1.44
8	0.16	1.64
10	0.13	1.69
14	0.09	1.6

Figs. 2 and 2a give the results graphically.

It will be noticed that the product  $N^2i^2$  is not constant for the air-core coils, although it tends to a constant value at the upper value of  $N$ , and is constant with the open iron and closed iron-core coils, although the value of  $N^2i^2$  is different in the latter two cases. In other words, the results may be said to be similar in kind to those obtained in Wheeler and Thornton's investigations.

The present investigation differs from those as recorded in the cited reports of Wheeler and Thornton, in that I have carried out measurements on the circuits after interruption. The first step consisted in the use of an arrangement as shown in Fig. 3. This is a Wheatstone bridge in conjunction with a ballistic galvanometer. The inductance coil  $a$ , non-inductive balance resistance  $b$ , ammeter  $c$ , flick contact breaker  $d$ , variable non-inductive resistance  $e$ , and battery  $f$  are all (excepting  $b$ ) as used in the explosion experiments.  $a$  and  $b$  are shunted by non-inductive resistances  $r$  of sufficiently low resistance to eliminate sparking at  $d$  when the circuit is broken. Using with each coil the current values required

to give the igniting sparks, the observed "kicks" were plotted against  $N$ . These are given in Fig. 4. The straight lines indicate that for each group the energy associated with the system prior to interruption was constant, but they give no information as to

FIG. 2.

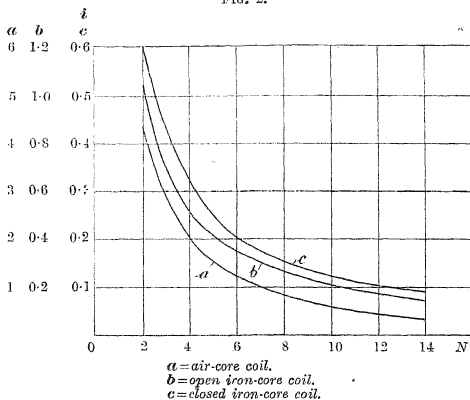
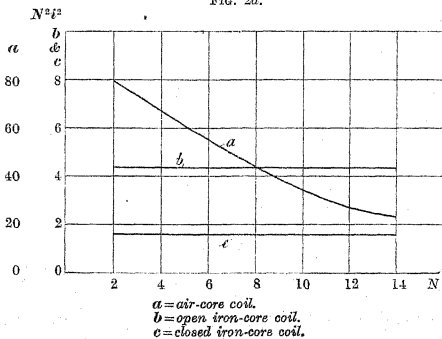


FIG. 2a.



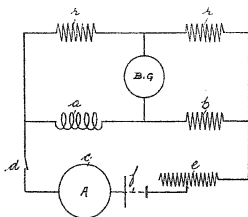
whether the energy was the same for each group. The inductances were therefore measured, and found to give  $\frac{1}{2}Li^2 = \text{constant}$  for each group, but different for different groups. As nothing is gained by quoting all the values of all the inductances, only the largest for each group is recorded in table VI.

TABLE VI.

	$L$ .	$\frac{1}{2}Li^2$ .
Air-core coil, 14 layer .....	0.01	0.0006 joule.
Open iron-core coil, 14 layer .....	0.07	0.0008 "
Closed iron-core coil, 14 layer .....	0.56	0.0023 "

It is clearly not permissible to conclude that the energy projected into the sparks in the explosion experiments is constant for a constant magnetic condition, but different when that condition

FIG. 3.



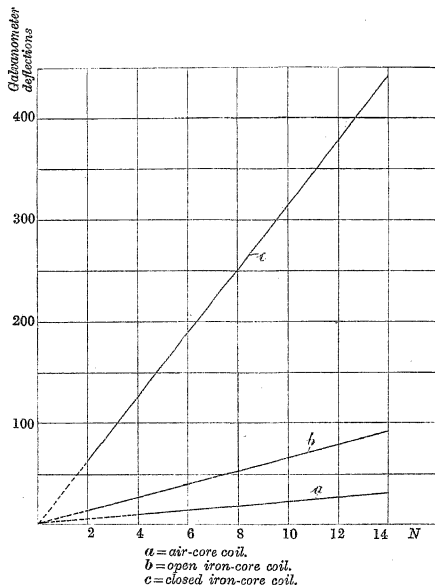
is changed, until it is proved that the differences found are not accounted for by core or other losses. A further step, involving direct spark measurements, was therefore necessary. After trying various schemes, the apparatus shown diagrammatically in Fig. 5 was adopted. *a* is the flick contact breaker used in the explosion experiments. This is enclosed in an ebonite chamber, *b*, to which a capillary tube is sealed. Two things appeared at first to render this device useless. The heat developed by the current passing through the contact breaker when closed was sufficient to interfere with proper measurement of the heating effect of the spark produced on opening the contact breaker. Further, it was difficult to maintain a perfectly gas-tight joint around the rotatable stem carrying the prong of the contact breaker. These troubles were avoided by permitting a slight leak in the chamber and observing (through a microscope) only the "kick" given to the liquid thread in the capillary tube. Using



the coils and current values employed in the explosion experiments, it was found that the "kicks" were the same throughout. It follows that the sparks obtained in the three widely varying groups of experiments were identical as regards their impulsive thermal effects.

I do not think it can be argued from the above that the spark

FIG. 4.

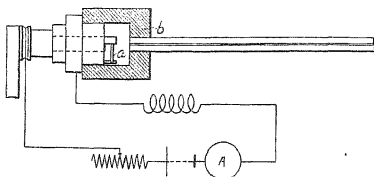


energy was the same in all cases, although this possibility is not excluded.

The final step consisted in an attempt to determine definitely whether the energies of the different sparks were the same or not. For this purpose, a high tension winding of fine wire and many turns was placed on one of the limbs of the closed iron core, as

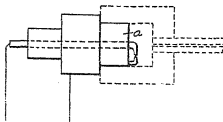
shown in dotted lines, Fig. 1, and connected to a small, permanent gap in a spark plug, *a*, Fig. 6. The sparks produced were very small, and several had to be produced in succession to give a deflection definitely readable through the microscope. In place of the flick contact breaker in the primary circuit, a cam-operated interrupter, such as is used in ignition apparatus for internal-combustion engines, was employed. With this interrupter, twelve

FIG. 5.



sparks were obtained from each complete rotation of the cam. The chamber was made perfectly gas-tight, and the deflections were different in character from those of the previous experiment in that they were relatively slow. Taking each of the coils in turn and using the current values obtained in the explosion experiments, the deflections obtained after one complete rotation of the cam were observed. In all cases they were found to be the same.

FIG. 6.



It follows that the total heating effect of the same number of sparks from each coil was the same; consequently, the sparks were of equal energy. Seeing that the sparks in all three groups of experiments gave the same impulsive thermal effects and the sparks in one group gave the same energy effects, it is permissible to argue that the energies of all the sparks in the three groups were the same.

The conclusion of the investigation is therefore that over the wide range of different conditions examined, the igniting sparks had this in common—that they all liberated the same amount of heat energy, a result which is not evident from measurements on the spark circuit prior to the production of the sparks.

Regarding single spark ignition of explosive gases initially at atmospheric temperature and pressure, the main results of investigations which have been published in recent years, and which can be regarded as well established, appear to be as follows:

(1) With a low tension spark, the least spark energy required to ignite a given gas mixture diminishes with increase of the voltage impressed on the spark circuit prior to the production of the spark (The least energy required to start a gaseous explosion, W. M. Thornton, *Phil. Mag.*, 1914, [vi], 28, 734).

(2) When the circuit voltage is constant, the spark energy required for ignition of a given gas mixture by a low tension spark is constant (see above).

(3) With a high tension spark (which consists of a capacity component preceding an inductance component), the incendency of the spark (or ability to cause ignition) can be increased by increasing the proportion of energy in the initial part of the spark without increasing the total energy of the spark ("Spark Ignition," J. D. Morgan, *Engineering*, November 3rd, 1916).

(4) The incendency of a condenser or capacity spark is greater than that of an inductance spark dissipating the same amount of energy (Thornton, *loc. cit.*).

(5) With a capacity spark, the least energy required for ignition of a given gas mixture diminishes as the spark voltage increases (Thornton, *loc. cit.*).

These results clearly establish the fact that the incendency of a spark does not depend on the total energy of the spark.

It is generally supposed that the energy required to produce ignition of a given inflammable gas mixture is constant for similar physical conditions. If the assumption is correct, then the fact that the total energy of the least igniting spark is found experimentally to vary with the conditions under which the spark is produced suggests that not all of the spark energy is utilised in the process of ignition, but only a portion at the commencement of the spark. It is, of course, possible that the inflammability of a gas as determined by the least energy required to produce ignition is not constant for identical physical conditions of the gas, but it would appear to be useless to attempt an investigation of this point by spark measurements having regard to the facts above mentioned. It is important to note that a spark is a varying

source of heat which very rapidly reaches its maximum intensity and then less rapidly disappears. Experiments prove that increase of the initial intensity of a spark results in increased incendivity. As already stated, this suggests that ignition is due only to the initial part of the spark, and that in every spark there is a certain amount of unused energy which makes no contribution to the process of ignition. The proportion of unused energy must diminish as the initial intensity increases, but at present any measurements of the effective portion of the spark appear to be impossible. It follows from this suggested theory of unused energy that any attempts to specify the inflammability of a gas in terms of the total energy of the least igniting spark must necessarily yield the diverse results which have hitherto been obtained.

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[Received, November 21st, 1918.]

### X.—*The Physical Constants of Nicotine. Part I.* *Specific Rotatory Power of Nicotine in Aqueous Solution.*

By HARRY JEPHCOTT.

NICOTINE has been purified and its constants have been recorded by Landolt ("Optical Rotation of Organic Substances"), Nasini and Pezzolato (*Zeitsch. physikal. Chem.*, 1893, **12**, 501), Gennari (*ibid.*, 1896, **19**, 130), Hein (*Diss.*, Berlin, 1896), Pribram and Glücksmann (*Monatsh.*, 1897, **18**, 303), Ratz (*ibid.*, 1905, **26**, 1241), and Winther (*Zeitsch. physikal. Chem.*, 1907, **60**, 563). All, with the exception of Ratz, relied on the distillation in hydrogen of anhydrous nicotine. Ratz utilised two methods, namely, fractional distillation in a vacuum and the formation of nicotine zinc chloride followed by distillation. Their results for the specific rotation, which show considerable variation, are as follows:

	$[\alpha]_D^{20}$	$D_4^{20}$
Landolt .....	161.55	1.01101
Nasini and Pezzolato .....	161.29	—
Gennari .....	162.84	1.01071
Hein .....	164.18	1.01049
Pribram and Glücksmann .....	164.91	1.0095
Ratz (by fractional distillation) .....	166.77	—
" (from double salt) .....	169.0 to 169.54	1.00925
Winther .....	163.85	—

It appeared probable that the variation was due to the presence of the alkaloids nicotine, nicotelline, and nicotimine, which occur with nicotine, and it was decided to purify nicotine by the method utilised by Pictet and Rotschy (*Ber.*, 1901, **34**, 696) when isolating these alkaloids. Nicotine which had been prepared from tobacco by steam distillation was dissolved in a slight excess of hydrochloric acid and treated with sodium nitrite at low temperature. The nicotine was subsequently liberated by alkali, dehydrated, and fractionally distilled under diminished pressure. Considerable loss of nicotine occurred owing to the formation of oxidation products during the treatment with nitrite.

A quantity, about 2500 grams in all, of commercial nicotine was also converted into nicotine zinc chloride, twice recrystallised, and the nicotine liberated, dehydrated, and fractionally distilled under diminished pressure in a manner similar to that of Ratz (*loc. cit.*).

The distillation was a source of much trouble. In the cold, nicotine readily forms highly-coloured oxidation products on exposure to the air. When hot, this oxidation is extremely rapid, and water is also absorbed. At the temperature of distillation, the vapour readily attacks cork or rubber used for connexions. Well-fitting ground-glass joints are essential, but there proved to be no necessity to flood the apparatus with hydrogen if a sufficiently high vacuum were maintained (20—40 mm. pressure).

The nicotine prepared in this way was colourless and almost without odour in the cold. When kept in bottles filled to the stopper and away from the light, nicotine remains colourless, only the slightest yellow tint being noticed after six months and no change in rotatory power (compare Pribram, *loc. cit.*, p. 303).

For pure nicotine, the density and rotatory power were found to be as follows:

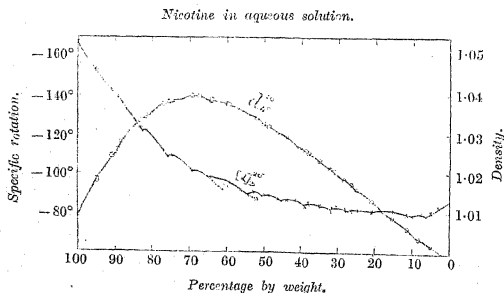
	$D_4^{20}$	$[\alpha]_D^{20}$
Purified through nitroso-compound .....	1.00920	168.52
Purified through double chloride (1) ...	1.00925	168.61
"    "    "    "    (2) ...	1.00925	168.40
"    "    "    "    (3) ...	1.00925	168.66

The three sets of figures for the double chloride method refer to three separate and distinct preparations of pure nicotine in that way.

Many dilutions of this nicotine with water were prepared, and the specific gravity and specific rotatory power for them observed. The rotations were measured with a Schmidt and Haensch half-shade polarimeter, using a tube having a length of 100.04 mm.

Per- centage by weight.	Grams in 100 c.c.	$D_4^{20}$	$[\alpha]_D^{20}$	Per- centage by weight.	Grams in 100 c.c.	$D_4^{20}$	$[\alpha]_D^{20}$
100	100.925	1.00925	168.61	44.004	45.296	1.02936	86.47
95.068	96.801	1.01823	153.06	41.718	42.882	1.02790	86.71
91.084	93.323	1.02458	141.65	40.237	41.308	1.02661	85.09
89.471	91.781	1.02583	138.73	38.798	39.804	1.02592	83.79
88.338	90.820	1.02810	134.11	38.065	39.025	1.02522	85.21
83.336	86.132	1.03356	123.21	37.986	38.950	1.02538	84.98
81.842	84.632	1.03439	121.48	35.098	35.920	1.02341	83.52
77.006	79.921	1.03784	111.47	34.877	35.696	1.02351	83.39
75.538	78.551	1.03836	108.39	32.141	32.810	1.02107	81.83
84.868	77.764	1.03839	108.69	30.973	31.607	1.02048	82.48
69.202	71.963	1.03990	100.47	30.637	31.253	1.02010	82.67
67.538	70.231	1.03988	—	30.291	30.915	1.02060	82.60
64.423	66.918	1.03890	97.82	28.151	28.664	1.01820	81.95
63.950	66.440	1.03894	95.63	26.473	26.930	1.01725	81.78
60.773	63.110	1.03846	94.02	24.975	25.369	1.01588	81.67
59.898	62.131	1.03728	93.69	20.963	21.235	1.01300	80.64
59.649	61.895	1.03765	95.12	20.726	20.995	1.01299	80.06
56.241	58.250	1.03614	91.27	15.023	15.156	1.00880	80.99
54.289	56.245	1.03603	89.27	12.963	13.027	1.00492	79.79
53.096	54.934	1.03463	90.12	11.508	11.579	1.00611	79.43
51.969	53.750	1.03428	86.91	10.012	10.061	1.00611	78.66
50.134	51.777	1.03278	89.03	9.921	9.971	1.00494	79.20
48.949	50.513	1.03194	88.19	7.417	7.441	1.00317	79.94
46.632	48.062	1.03065	86.23	6.604	6.622	1.00276	79.25
46.183	47.629	1.03131	—	4.998	5.006	1.00153	80.48
46.015	47.412	1.03037	86.79	2.505	2.504	0.99970	83.15

The effect of temperature on the density and rotatory power both of pure nicotine and certain of its aqueous solutions has also been observed. For this purpose, a jacketed polarimeter tube was



employed, a Sprengel tube being used for the densities. It was not convenient in every case to observe both density and angle at the same temperature, and the density at the temperature at

which the rotatory power was observed was obtained from a graph constructed from the recorded densities.

*Pure Nicotine.*

Temperature.	20°.	21.1°.	40°.	60°.	80°.	97.7°.
$D_4^{20}$ .....	1.00925	1.00865	0.99424	0.97799	0.96184	0.94534

Temperature.	$D_4^t$ (from graph).	$[\alpha]_D^{20}$ .
20°	1.00925	168.20°
29.5	1.0017	168.71
41.5	0.9924	169.09
52	0.9840	169.51
62	0.9760	169.74
69.6	0.9699	169.94
86.4	0.9567	169.73
92.0	0.9521	169.71

Owing to the so-called closed curve of solubility of nicotine in water, it is not possible to observe the rotatory power and density of solutions containing between 7 and 87 per cent. of nicotine at all temperatures up to 100°, since separation occurs at about 60°. Two solutions were therefore prepared which would fall outside this closed curve, and contained 6.638 per cent. and 88.338 per cent. of nicotine. For these, the following figures were found:

Temperature.	Percentage by weight.	Grams in 100 c.c.	$D_4^t$ .	$[\alpha]_D^{20}$ .
20° .....	6.638	6.682	1.00275	76.82
85 .....	6.638	6.4188	0.96328	95.29
20 .....	88.338	90.820	1.02810	134.16
90 .....	88.338	86.936	0.98412	150.34

It will be observed that the change in rotatory power is marked.

On cooling to 20°, the 6 per cent. solution at once showed its original rotatory power, but the 88 per cent. solution did not revert to its former value for some days, although an immediate fall to about  $[\alpha]_D^{20}$  138.0 took place. Difficulty occurs in determining the rotatory power of pure nicotine and its more concentrated solutions, since, owing presumably to light absorption, it is necessary to match a greyish-pink against a grey when taking polarimetric readings. In the case of the more concentrated aqueous solutions, the difficulty is greatly increased owing to the very marked changes in density. In observing the angle of the 88 per cent. solution at 90°, even with a rapid stream of water circulating round the jacket, the change in density by cooling at the exposed surface of the end plates was so marked as to make it almost impossible to get light to pass through the tube, and the

rotation recorded must be considered liable to an error of  $1^{\circ}$ . No such difficulties were experienced with the 6 per cent. solution.

The graphs for density and specific rotatory power of nicotine in aqueous solution both exhibit a series of maxima, and these agree with molecular proportions of nicotine and water. This indication of the formation of a series of hydrates is confirmed by an examination of the freezing points of nicotine solutions.

Between 40 and 80 per cent., the time taken for hydrate-formation is appreciable, and the abnormal points marked were found in cases of solutions when the rotation was observed immediately after mixing. A solution containing 69.2 per cent. of nicotine showed no change in rotation after keeping for twelve months.

*The "Closed Curve of Solubility" for Nicotine.*

The formation of hydrates of nicotine and their decomposition at higher temperatures shows the true nature of the "closed curve of solubility." Nicotine is only sparingly soluble in water, and water is only sparingly soluble in nicotine, but hydrates of nicotine are miscible with either, a state of balance existing at any given temperature between nicotine, its hydrates, and water.

When the temperature rises, the hydrate-formation reverses, and on the concentration of free nicotine becoming greater than the solubility of nicotine in water at that temperature, separation occurs. By choosing concentrations of nicotine and water such that the limit of solubility of the one in the other was not exceeded, it was possible, as shown above, to note the marked rise in rotatory power as the concentration of free nicotine increased with the rise in temperature, and it is to be expected that with convenience for observing the angle at a sufficiently high temperature, the true rotatory power of nicotine in water would be obtained.

I am indebted to Mr. George Dean, Head of the Chemistry Department of the Institute, for valuable suggestions and advice, and to the Chemical Society for a grant towards the cost of this research.

WEST HAM MUNICIPAL TECHNICAL INSTITUTE.

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## XI.—*The Sub-acetate and Sub-sulphate of Lead.*

By HENRY GEORGE DENHAM.

IN recent papers the author has shown how lead sub-oxide may be converted into the sub-haloid salts by the action of alkyl haloid vapour (T., 1917, 111, 29; 1918, 113, 249); in the present paper a somewhat similar method has been used for the preparation of lead sub-acetate and sub-sulphate.

In all these experiments, the lead sub-oxide was prepared by the decomposition of pure lead oxalate according to the method previously described (*loc. cit.*). The same precautions have been followed in order to secure thorough preliminary heating of the reacting gases, the vapour being passed through a capillary spiral tube contained in the oven before it came in contact with the sub-oxide. The only modification necessary in the distillation has been that no drying agent was used in the apparatus, and it was necessary to heat electrically all the leading tubes in order to prevent undesired condensation and to secure a steady rate of distillation.

### *Preparation of Lead Sub-acetate.*

Preliminary experiments were carried out with methyl acetate. About 10 c.c. of a carefully dried sample of this substance were distilled through about 0.75 gram of lead sub-oxide, the duration of the experiment being approximately ninety minutes. Analysis of the product indicated that at 310° the sub-acetate decomposes completely, metallic lead being formed, whilst at temperatures much below this, the reaction proceeded too slowly to appear promising. Ethyl acetate behaved similarly, and an experiment was then carried out with acetic anhydride.

Lead sub-oxide mixed with about four times its weight of powdered glass was prepared in two bulbs (for details, see T., 1917, 111, 29), and the apparatus filled with oxygen-free nitrogen. About 8 c.c. of carefully fractionated acetic anhydride were distilled through the bulbs at 195°, as recorded on a standardised platinum thermometer. This slow distillation generally lasted about eighty to ninety minutes. The oven was then cooled to about 180°, and the apparatus was exhausted by means of a Sprengel pump. The bulbs were then sealed off and were available for analysis. By this

procedure, any trace of acetic anhydride could be removed from the bulb without causing any decomposition of the sub-acetate.

One difficulty still remained. Traces of water were found to be retained most tenaciously by the sub-acetate. A few samples which were quite free from moisture were prepared, but in general, although the ratio of lead to acetate in the compound agreed with the theoretical ratio for lead sub-acetate, from 1 to 3 per cent. of water was also present. The presence of the water was repeatedly verified by the action of heat, a liquid which rendered anhydrous copper sulphate blue being fairly readily expelled.

Traces of acetic acid were generally present in nearly all the samples of acetic anhydride used, and this probably accounted for the presence of water in the sub-acetate. However, as the anhydrous and the hydrated sub-acetate showed no difference in solubility and general properties, anhydrous acetic anhydride was used only in certain control experiments.

Found: Pb=77.6, 77.9, 77.9;  $C_2H_3O_2=22.3, 22.0, 22.2$ .

$CH_3 \cdot CO_2Pb$  requires Pb=77.82;  $C_2H_3O_2=22.18$  per cent.

In seven experiments made with acetic anhydride containing traces of acetic acid, the average of the analyses was Pb=75.8;  $C_2H_3O_2=21.5$ . There is a possible hydrate of the formula  $(CH_3 \cdot CO_2Pb)_2 \cdot H_2O$  which contains Pb=75.3 per cent., and it appears probable that where acetic anhydride containing traces of acetic acid is used, the product is the hydrate, containing more or less of the anhydrous sub-acetate. Thus in two experiments, in which the same sample of acetic anhydride was used, after a distillation lasting ninety minutes, the percentage of lead was: (a) bulb 1, 75.4, bulb 2, 75.2; (b) bulb 1, 75.1, bulb 2, 75.2.

#### *Properties of the Sub-acetate.*

In order to obtain evidence of the existence of the sub-acetate, determinations of the conductivity of a saturated solution of the substance and of the normal dehydrated acetate were carried out in absolute alcohol at 25°. The apparatus and method previously described (*loc. cit.*) were again used in order that traces of oxygen might be excluded when the sub-acetate was used. The resistance of the alcohol was 90,000 ohms, whilst that of a saturated solution of the normal acetate was 4100 ohms, and of the sub-acetate, (a) 6100, (b) 6400, (c) 6000 ohms.

As further evidence of the existence of a definite sub-acetate of lead, experiments on the decomposition of the normal acetate and the sub-acetate were undertaken. A sample of the anhydrous

normal acetate was heated in a vacuum and the temperature slowly raised. At  $200^{\circ}$ , a very slow evolution of gas occurred, becoming rather brisker at  $240^{\circ}$ . The temperature was then kept constant and the pump kept in action for nineteen hours. Gas was still very slowly evolved, and it was found that the acetate had scarcely changed colour, and there was a considerable crop of long, white, needle-like crystals which had volatilised out of the bulb into the relatively cooler leading tube within the oven.

A sample of the sub-acetate was then similarly treated. At  $200^{\circ}$ , gas was slowly evolved, the evolution becoming brisker at  $240^{\circ}$ . After seven hours at  $240^{\circ}$ , gas was still being evolved slowly, and a small, volatilised band of white, amorphous, basic material was found outside the furnace, whilst the material in the bulb had undergone a marked change. It was now full of long, needle-like, greyish crystals. This change, from a finely crystalline, bluish-grey substance into a mass of grey, needle-like crystals, was very marked, as, too, was the entire absence of the volatilised, white, needle-like crystals obtained in the decomposition of the normal acetate. The behaviour on heating the different acetates in a vacuum is so different that it would be difficult to maintain the view that the sub-acetate is a heterogeneous mixture of metal and normal acetate, and these results, coupled with the different conductivity of the saturated solutions, must rather be held to confirm the view of the chemical individuality of the sub-acetate. The sub-acetate exhibits the same behaviour towards acids as other sub-salts of lead, namely, it is rapidly decomposed into metal and normal salt.

#### *Lead Sub-sulphate.*

Methyl sulphate was distilled through lead sub-oxide at  $280^{\circ}$  for about seventy-five minutes, the manipulation being similar to that already described for the sub-haloid salts of lead (*loc. cit.*). No difference in behaviour or in appearance was detected in the products prepared from lead sub-oxide or from the sub-oxide diluted with four times its weight of silica. On the other hand, when the distillation was carried out at  $310^{\circ}$ , and the silica omitted, the resulting grey mass was seen under the microscope to contain clusters of white crystals in a dark background, and was clearly heterogeneous.

In the sub-sulphate prepared according to the above method, the lead was estimated by conversion into lead sulphate, and the sulphate by treating the sub-salt with dilute nitric acid, evaporating to dryness, washing out the lead nitrate, and weighing the

residue in a Gooch crucible as lead sulphate. Owing to the presence of traces of carbonaceous matter, the precipitate was generally faintly grey until after gentle ignition.

Found: Pb=81.25, 81.62, 81.30, 81.29;  $\text{SO}_4$ =18.65, 18.56, 18.80, 18.62.

$\text{PbSO}_4$  requires Pb=81.18;  $\text{SO}_4$ =18.82 per cent.

#### *Properties of the Sub-sulphate.*

The action of acids on the sub-sulphate is similar to their action on the sub-haloid salts. A solution of ammonium acetate when boiled with the substance leaves a deposit of spongy lead. In order to test the chemical individuality of a saturated solution of the salt, determinations of the conductivity in water and alcohol at 18° were made. The resistance of the water was 27,000 ohms, whilst that of a saturated solution of lead sulphate was 3030 ohms, and that of the sub-sulphate was (a) in air, 3100 ohms, and (b) in a vacuum, 3200 ohms.

The difference is so slight that it appears highly probable that there is decomposition into lead and lead sulphate, although no visible change occurred in the appearance of the residue.

The resistance of the alcohol was 90,000 ohms, whilst that of a saturated solution of lead sulphate was 93,000 ohms, and of the sub-sulphate 75,000 ohms.

Although a much more marked difference was obtained, the evidence afforded by the conductivity method was still so inconclusive that further evidence as to the individuality of the salt was sought by investigating the influence of temperature on the sub-sulphate. Were the substance a heterogeneous mixture of lead and lead sulphate, a rise in temperature above the melting point of lead would be expected to cause a pronounced change in the appearance of the finely divided lead. Before heating the sample, some of it was carefully observed under the microscope, and no sign whatever of heterogeneity was noticed, but the whole appeared a uniform iron-grey. The temperature was raised 120° above the melting point of lead for a period of four hours. On cooling, the microscope failed to reveal any change whatsoever in the appearance of the salt. The entire absence of anything in the nature of minute globules of lead certainly supports the contention that this greyish substance is definitely lead sub-sulphate.

#### *Conclusion.*

- (1) Lead sub-acetate has been obtained by the action of acetic anhydride on lead sub-oxide at 195°.

(2) The substance is bluish-grey, and behaves similarly to other sub-salts of lead.

(3) Its solubility in alcohol differs slightly from that of the normal acetate, but the behaviour of the two acetates on heating in a vacuum supports the view of the chemical individuality of the sub-acetate.

(4) The sub-sulphate has been prepared by the action of methyl sulphate vapour on the sub-oxide at  $280^{\circ}$ .

(5) The substance is dark grey; conductivity experiments indicate that it decomposes on solution in water, but it appears more soluble in alcohol than does the normal sulphate.

(6) On heating the substance  $120^{\circ}$  above the melting point of lead, no change in its appearance could be detected or any sign of globules of lead.

In conclusion, the author begs to thank the Walter and Eliza Hall Trust for the facilities placed at his disposal for the prosecution of this work.

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## XII.—*The Synthesis of Ammonia at High Temperatures. Part III.*

By EDWARD BRADFORD MAXTED.

IN previous communications (T., 1918, 113, 168, 386), some account has been given of the formation of ammonia in a rapidly cooled high-tension arc and in water-cooled flames, and evidence has been brought forward to show that the percentage of ammonia in equilibrium with nitrogen and hydrogen, after decreasing with increasing temperature, passes through a minimum value, and at very high temperatures increases with increasing temperature, a result which may also be shown thermodynamically.

A determination of the equilibrium ammonia-content at the temperature of the high-tension arc (*J. Soc. Chem. Ind.*, 1918, 37, 232) gave approximately 1.7 per cent. by volume for the equilibrium percentage at atmospheric pressure under the experimental conditions employed, and yields of ammonia up to 1.5 per cent. could be recovered by suitable cooling.

This reversal in the direction of variation of the equilibrium ammonia-percentage with temperature appears to be sufficiently interesting to justify further study, and it is proposed in the present paper to deal with the formation of ammonia in an arc of larger size and more usual character than those hitherto employed.

For the production of the arc, single-phase, 50-cycle alternating current supplied at a maximum potential of 375 volts was transformed to high tension by means of an oil-immersed static transformer having a step-up factor of 31.5.

It was found easily possible to obtain an appreciable concentration of ammonia by almost any method by which the mixture of nitrogen and hydrogen was brought into contact with the arc flame with subsequent rapid cooling, for instance, by means of a blown arc similar to that used by McDougall and Howles (*Proc. Manchester Phil. Soc.*, 1900, **44**, No. 13) for the synthesis of nitric oxide, but in such cases a considerable proportion of the gas mixture blown into the arc failed to reach the requisite uniform high temperature, and for a preliminary study of the maximum percentage of ammonia formed, as distinguished from the maximum quantity formed with a given expenditure of electrical energy, it was considered preferable to allow the arc to burn freely in the reacting gas mixture and to draw off samples of gas by means of a silica tube of small diameter placed in close proximity to the arc.

The latter part of the present paper was carried out with a view to bringing additional evidence that the formation of ammonia at high temperatures really takes place by the direct union of hydrogen and nitrogen, and not by the subsequent reduction of nitric oxide formed from traces of oxygen in the reacting gases.

It should, further, be stated in this connexion that the mixture of nitrogen and hydrogen employed in all experiments reported both in this and in the previous papers was as far as possible free from oxygen, and in no case contained sufficient of this to account for such secondary formation of any appreciable part of the ammonia obtained.

#### EXPERIMENTAL.

The apparatus employed is shown in the figure. The electrodes *A* and *B* are of platinum, and terminate in small spheres slightly more than 1 mm. in diameter. *C* is a thick-walled capillary silica tube, its upper end being opened out and flattened so as to form a slit approximately 4 mm. long and 1.5 mm. wide. The silica

wall bounding the ends of this was ground away, and in the depressions thus formed at each end of the silica slit, the electrodes rested, the lower part of the tube being circular in section and about 1.5 mm. in internal diameter.

The arc was enclosed in a large inverted flask provided with a side-tube and three-way tap, *D*, for preliminary exhaustion and subsequent admission of the gas to be subjected to the action of the arc, this gas normally passing into the flask at *D* and leaving the system by way of the silica tube already described.

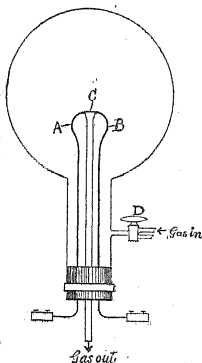
For the following measurements, the current employed for arc-formation was limited by the interposition of an adjustable resistance on the low-tension side of the transformer.

The platinum electrodes became quickly white hot and the arc flame burned steadily across the slit, and was, to a certain degree, drawn into the tube by the current of gas. Sufficient cooling for the recovery of the greater portion of the ammonia formed and for the prevention of the fusion of the silica tube was obtained without water-cooling, provided that a thick-walled silica capillary was used and that the arc employed was not too large.

Samples of gas, taken at various rates, were analysed by passage through *N*/10-acid, and in some cases by allowing a small volume to pass through Nessler's solution, practically identical results being obtained from each method of analysis.

The quantity of ammonia observed is influenced necessarily, not only by the temperature of the arc, but also by heating and cooling factors. With very slow currents of gas, heating to arc temperature occurs satisfactorily, but the ammonia formed undergoes considerable decomposition owing to the slowness with which it leaves the region of maximum temperature. Passage of the gas too quickly through the arc results in imperfect heating, such rapid passage, however, involving rapid cooling, and consequently a more complete retention of the ammonia formed.

It will be seen from table I that the concentration of the ammonia recovered at the ordinary temperature first of all rises rapidly with increasing velocity of passage, then passes a maximum



value, the percentage of ammonia subsequently falling gradually with still greater velocities of passage. This form of the concentration-velocity curve is a necessary result of the nature of the heating and cooling factors discussed above.

The issuing gas, of course, had a strong odour of ammonia at all the rates of flow studied, and the percentages obtained were of the same order of magnitude as those previously observed with small arcs not produced directly by a high-tension current of the usual sinusoidal wave form. For this series of experiments, 0.04 ampere at a potential of 3250 volts was taken for arc-formation.

TABLE I.

*Gas Mixture: Nitrogen, 25 per cent.; Hydrogen, 75 per cent.*

Rate of flow of gas in litres per hour.	Concentration of ammonia per cent. by volume.	Rate of flow of gas in litres per hour.	Concentration of ammonia per cent. by volume.
0.5	0.49	3.4	0.49
0.57	0.6	(3.4	0.45)
0.85	1.2	4.6	0.43
1.14	1.04	6.1	0.40
2.1	0.58	7.5	0.36
(2.1	0.56)	(7.5	0.32)

It appears desirable at this point to discuss the evidence that the formation of ammonia at high temperatures takes place by the direct union of nitrogen and hydrogen, and not secondarily by the reduction of nitric oxide formed from nitrogen and traces of oxygen in the reacting gas. The point is of fundamental importance in any consideration of the variation of the ammonia equilibrium with temperature, and for this reason has been examined in such a way as to place beyond doubt the direct nature of the synthesis of ammonia at arc temperatures.

It may easily be shown from a consideration of the nitric oxide equilibrium, particularly on account of the small partial pressure of the nitrogen in the gas mixture employed, such mixture consisting uniformly of 25 per cent. of nitrogen and 75 per cent. of hydrogen, that a trace of oxygen, amounting to 1 per cent. by volume or less, will not account for the percentage of ammonia obtained, even assuming that all the nitric oxide which can be formed under the conditions of experiment is quantitatively reduced to ammonia. The amount of nitric oxide that can be formed from nitrogen and oxygen at partial pressures of the order mentioned is depressed, by the ratio of partition of oxygen between hydrogen and nitrogen, to a very small fraction of the already



small percentage which may be calculated as capable of being formed from a consideration of the nitric oxide equilibrium only.

In spite, however, of the small order of magnitude of the percentage of ammonia that might be formed secondarily from the traces of oxygen which are always present in commercial gases, it was considered preferable, both for the work described in the present paper and for all measurements of the formation of ammonia at arc temperature previously reported, to employ a gas known to be free from oxygen within the limits of the ordinary methods of analysis.

This gas was prepared in a manner similar to that used by Haber and Van Oordt (*Zeitsch. anorg. Chem.*, 1905, **44**, 341) for their determinations of the ammonia equilibrium at lower temperatures in the presence of a catalyst, by decomposing ammonia by passage through a heated iron tube, the mixture of nitrogen and hydrogen produced being carefully and thoroughly freed from ammonia by treatment with sulphuric acid and compressed for convenience into a previously exhausted steel cylinder by means of a totally immersed compressor of such design as to render impossible any penetration of air to the gas during compression. Each cylinder of nitrogen and hydrogen prepared in this way was carefully tested for absence of ammonia before use, by bubbling a considerable volume through Nessler's solution. The gas-mixture contained certainly less than 0.1 per cent. of oxygen, from which percentage the ammonia capable of being formed secondarily would be negligible, and in any case incapable of accounting for a yield of ammonia of 1 per cent. or more.

In a few preliminary measurements, a gas was used which had been made by the catalytic removal of traces of oxygen from a mixture of commercial hydrogen and nitrogen by passage over a heated metal, but whilst the resulting gas was equally satisfactory from the point of view of the yield of ammonia obtained by passage through an arc, the preparation of an oxygen-free mixture in this way was more troublesome than by the first method.

In addition to employing a gas free from oxygen, it was considered interesting to examine the synthesis at arc temperature under such conditions that the same volume of nitrogen and hydrogen was repassed a number of times through the arc, the ammonia formed at each passage being absorbed and measured. It is obvious that any trace of oxygen would, particularly by reason of the hydrogen present, be removed during the first few passages through the arc, and that the conversion to ammonia of an approximately constant percentage of the gas-mixture during

each successive passage would confirm beyond doubt the direct nature of the synthesis.

The experimental method employed consisted in confining a known volume of an oxygen-free mixture of nitrogen and hydrogen in a graduated vertical glass capillary tube about 1 metre long. The upper end of this tube was fused on to a second, short, horizontal capillary tube containing platinum wire electrodes 0.5 mm. apart, between which a small induction arc, as described in a previous communication, could be formed, this second capillary tube ending in a small absorption pipette filled with dilute sulphuric acid. The lower end of the graduated capillary tube was sealed by means of mercury covered with a small quantity of sulphuric acid, and, by the regulated motion of this seal up and down the graduated tube, the thread of gas could be passed and repassed through the arc as often as desired. An approximately uniform rate of passage was obtained by making the graduated capillary tube one limb of a U-tube and causing the required motion by means of a mercury flow, this being normally regulated so that each double passage through the arc occupied about six minutes when 1 c.c. of the gas mixture was taken for experiment.

Working as above described, the ammonia formed during each upward passage was removed by the small absorption pipette sealed to the other end of the short capillary arc tube, whilst that produced during each downward passage was absorbed by sulphuric acid clinging to the side of the graduated capillary. The arc tube was, of course, not allowed to become wet on account of the danger of fracture, and the thread of gas, after its introduction, passed no joints by means of which penetration of air might occur.

Table II summarises the results obtained in two experiments of this nature, the estimation of ammonia being in this case carried out volumetrically by noting the contraction after each passage. A preliminary small expansion occurred on starting the arc, and passage was only begun after the volume had become more or less constant.

The yields of ammonia are much the same as those previously found for such arcs by other methods of analysis and with more accurate control over the rate of passage. Probably, by reason of the more rapid nature of the cooling, the yields are slightly higher than those obtained with the larger arc described in the first part of the present paper. Each cm. of the graduated capillary corresponded with 0.01 c.c. of gas, so that the volume could be read off with fair accuracy to 0.001 c.c.

TABLE II.

No. of expt.	Vol. of gas passed through arc. c.c.	No. of passages since beginning of expt.	Contraction after double passage through arc. c.c.	Percentage of ammonia formed.
1	0.74 (original volume) }	2	0.025	1.7
	0.715	4	0.025	1.7
	0.69	6	0.02	1.5
	0.67	8	0.025	1.9
	0.645	10	0.018	1.4
	0.627	12	0.022	1.8
	0.605	14	0.015	1.2
	0.59	16	0.02	1.7
2	0.825 (original volume) }	2	0.03	1.8
	0.795	4	0.025	1.6
	0.77	6	0.02	1.3
	0.75	8	0.027	1.8
	0.723	10	0.023	1.6
	0.70	12	0.02	1.4
	0.68	14	0.025	1.8
	0.655	16	0.025	1.9
	0.63	18	0.025	2.0
	0.605	20	0.01	0.8
	0.595	22	0.02	1.7
	0.575	24	0.02	1.7
	0.555	26	0.023	2.0
	0.532	28	0.022	2.0
	0.51	30	0.02	1.9
	0.49	32	0.015	1.5
	0.475	34	0.015	1.6

The experimental conditions, including control of rate of flow and the method of analysis, were not suitable for very accurate measurements, but the approximate constancy of the yield of ammonia, and especially the absence of any indication that a normal amount of ammonia is formed during the first passage and little or none during subsequent passages, appears to demonstrate without doubt the direct nature of the synthesis at high temperatures.

[Received, December 23rd, 1918.]

### XIII.—*The Effect of some Simple Electrolytes on the Temperature of Maximum Density of Water.*

By ROBERT WRIGHT.

ROSETTI (*Ann. Chim. Phys.*, 1867, [iv], 10, 461; 1869, 17, 370) has given a fairly exhaustive account of the early work carried out

on the determination of the temperature of maximum density of water and of a few salt solutions. A considerable portion of this work is due to Despretz (*Ann. Chim. Phys.*, 1839, [ii], 70, 49; 1840, 73, 296), and the most important result is embodied in the following law named after that investigator: "The lowering of the temperature of the point of maximum density of water caused by the addition of a solute is directly proportional to the concentration of the latter."

An attempt was made by Rosetti to connect the lowering of the temperature of maximum density brought about by the addition of a solute with the lowering of the freezing point produced by the same cause, but it was found impossible to formulate any general law, for although the ratio of the two lowerings was constant for any given solute at different concentrations, still a different ratio was obtained by the use of a second solute. In other words, whilst the lowering of the freezing point—being connected with the osmotic pressure of the solution—depends only on the concentration of the solute molecules, the lowering of the point of maximum density depends on the nature as well as on the number of dissolved molecules.

Coppet, in a series of researches (*Ann. Chim. Phys.*, 1894, [vii], 3, 246, 268; *Compt. rend.*, 1897, 125, 533; 1899, 128, 1559; 1900, 131, 178; 1901, 132, 1218; 1902, 134, 1208), has determined the molecular lowering of the temperature of maximum density for a number of salts of the alkalis, that is, the lowering produced by a gram-molecule of salt per litre, and the following table contains the more important of his results:

TABLE I.

	Chloride.	Bromide.	Iodide.
Rubidium .....	11.7	13.2	15.6
Potassium.....	11.6	12.8	15.4
Sodium .....	13.2	14.5	17.0
Lithium .....	6.0	7.0	8.3
Ammonium .....	7.2	8.7	11.1

From an examination of these figures, Coppet points out that of the three acid radicles, the iodide has the greatest and the chloride the least effect, and as a general conclusion states that: "Le rapport entre les abaisséments produit par le chlorure et le bromure (ou le bromure et le iodure) du même métal est sensiblement le même pour tous les métaux du groupe." The ratio varies between the values 0.78 and 0.91.

From the results of the present investigation, carried out with

monobasic inorganic acids and their salts with univalent metals, it will be shown that the lowering produced by any given salt conforms to a simple general rule, and can, in fact, be calculated from the known lowerings produced by other salts. The results of the measurements are given in table II, which contains the figures obtained for solutions varying in strength between semi- and one-sixteenth-molecular, the normal, or molecular lowerings, being calculated from those of lower concentration.

TABLE II.

*Lowering of the Temperature of Maximum Density of Salt Solutions.*

	<i>M</i> /16.	<i>M</i> /8.	<i>M</i> /4.	<i>M</i> /2.	Molecular lowering.
HCl .....	—	0·7	1·3	2·6	5·2
LiCl .....	—	—	1·4	2·8	5·6
NaCl .....	—	1·6	3·1	6·2	12·4
KCl .....	—	1·4	2·8	5·5	11·0
NH <sub>4</sub> Cl .....	—	1·0	1·8	3·6	7·2
HBr .....	—	0·9	1·8	3·7	7·4
LiBr .....	—	—	1·9	3·8	7·6
NaBr .....	—	1·8	3·7	7·4	14·8
KBr .....	—	1·6	3·2	6·5	13·0
NH <sub>4</sub> Br .....	—	1·2	2·3	4·7	9·4
HI .....	—	1·2	2·2	—	8·8
LiI .....	—	1·2	2·3	—	9·2
NaI .....	1·0	2·0	4·0	—	16·4
KI .....	0·9	1·8	3·7	—	14·8
NH <sub>4</sub> I .....	0·7	1·4	2·7	—	10·8
HNO <sub>3</sub> .....	0·8	1·6	3·1	—	12·4
LiNO <sub>3</sub> .....	—	1·6	3·1	—	12·4
NaNO <sub>3</sub> .....	1·3	2·5	5·0	—	20·0
KNO <sub>3</sub> .....	1·1	2·2	4·5	—	18·0
NH <sub>4</sub> NO <sub>3</sub> .....	0·9	1·8	3·6	—	14·4

It will be seen at once that the results agree with the law of Despretz, the semi-molecular solutions giving twice the depression of the corresponding fourth-molecular. Further, it is obvious that the lowering is not connected with the osmotic pressure, as the values shown for the molecular lowerings of different solutes vary greatly; nor is a consideration of the difference in the degree of ionisation sufficient to account for this abnormality, since the various solutions of any given concentration are practically ionised to the same extent.

The regularity running through all the measurements can readily be seen if the difference between the lowering shown by any acid and, say, its sodium salt is considered. This difference for the four

acids tabulated has the values 7.2, 7.4, 7.6, and 7.6; thus the replacement of the hydrogen ion by sodium causes a practically constant increase in the molecular lowering. A similar increase is found when potassium is used instead of sodium, the average value being 5.75, whilst for ammonium the value is 3.0. Further, the same effect is observed in the case of the acid radicle; thus, the replacement of chlorine by bromine increases the molecular lowering by 2.1, whilst the substitution of iodine for chlorine causes an increase of 3.7.

From a consideration of these results, it is evident that each acidic or basic radicle has its own effect on the lowering of the point of maximum density, and that the effect produced by a salt is equal to the sum of the lowerings caused by the metallic and acidic radicles. Hence, if we take the molecular lowering of hydrochloric acid—which gave the smallest effect of all the substances examined—as standard, we can obtain the molecular lowering of any salt or acid by the addition of two numbers, one corresponding with the acidic and the other with the basic radicle of the salt. It will at once be seen that there is a close resemblance between the above conclusion and Valson's law of moduli, which states that the density of a normal salt solution is the sum of an acidic and a basic effect, and can, in fact, be calculated by adding to the density of a normal solution of a standard substance—ammonium chloride—two figures or moduli, one characteristic of the acidic and the other of the basic radicle of the salt.

The moduli for the lowering of the point of maximum density are given in table III, and the molecular lowering of any salt can be found by adding to the molecular lowering of hydrochloric acid (5.2) the two moduli corresponding with the given salt. For example, the calculated lowering for potassium nitrate would be  $5.2(\text{hydrochloric acid}) + 5.75(\text{potassium}) + 7.2(\text{nitrate}) = 18.15$ , the actual value found being 18.0. Several values for each modulus calculated from different salts are shown in the table, together with the mean value derived from them.

TABLE III.

	Cl.	Br.	I.	NO <sub>3</sub> .	Average.	
Li .....	0.6	0.2	0.4	0.0	0.3	
Na .....	7.2	7.4	7.6	7.6	7.45	
K .....	5.8	5.6	6.0	5.6	5.75	
NH <sub>4</sub> .....	2.0	2.0	2.0	2.0	2.0	
	H.	Li.	Na.	K.	NH <sub>4</sub> .	Average.
Br .....	2.2	2.0	2.4	2.0	2.2	2.2
I .....	3.6	3.6	4.0	3.8	3.6	3.7
NO <sub>3</sub> .....	7.2	6.8	7.6	7.0	7.2	7.2

It should be noted that a similar set of moduli could be calculated from the molecular lowerings given by Coppet, although as a rule his values would not be identical with those tabulated; the results, however, approximate to one another fairly closely considering the difference in the experimental methods employed.

We may next consider the results obtained with the weak monobasic organic acids in comparison with their highly ionised salts. Formic, acetic, and propionic acids, together with their sodium and ammonium salts, have been examined.

TABLE IV.

	<i>N</i> /8.	<i>N</i> /4.	<i>N</i> /2.	<i>N</i> .
Formic acid .....	—	1.7	3.6	7.2
Na salt .....	1.6	3.2	—	12.8
NH <sub>4</sub> salt .....	—	1.7	3.6	7.2
Acetic acid .....	—	1.8	3.7	7.4
Na salt .....	1.5	3.0	—	12.0
NH <sub>4</sub> salt .....	—	1.6	3.1	6.2
Propionic acid .....	—	2.0	4.0	8.0
Na salt .....	1.5	3.0	—	12.0
NH <sub>4</sub> salt .....	—	1.7	3.4	6.8

The results do not show the normal change, 7.6, which was obtained with strong acids when the hydrogen atom was replaced by sodium, but the difference between the values for the sodium and ammonium salts is constant in all three cases and is identical with that obtained in the case of the inorganic acids. In other words, the highly ionised salts of organic acids behave in the normal manner, whilst the feebly ionised acids themselves are abnormal.

The dibasic acids, with their acid and neutral salts, are also of interest.

TABLE V.

	<i>M</i> /16.	<i>M</i> /8.	<i>M</i> /4.	<i>M</i> .
Sulphuric acid .....	—	3.0	6.1	24.4
NaH salt.....	2.0	4.0	—	32.0
Na <sub>2</sub> salt .....	2.0	4.0	—	32.0
Oxalic acid .....	—	1.5	3.0	12.0
NaH salt.....	—	2.4	—	19.2
Na <sub>2</sub> salt .....	2.0	4.0	—	32.0
Succinic acid .....	—	1.7	3.4	13.6
NaH salt.....	—	2.5	—	20.0
Na <sub>2</sub> salt .....	1.5	2.9	—	23.2

It will be seen that the replacement of one hydrogen atom by

sodium in the two stronger acids gives values approximating to the normal, whilst succinic acid gives a slightly lower value, thus resembling the weak monobasic acetic and propionic acids. In all cases, the replacement of the second hydrogen atom is quite abnormal and differs widely in the three cases. From the normal behaviour of the acid salt, it may be concluded that the ions of sodium hydrogen sulphate consist mainly of  $\text{Na}^+$  and  $\text{HSO}_4^-$ , and not  $\text{H}^+$  and  $\text{NaSO}_4^-$ . It should be noticed that as the greatest concentration examined in these acids was  $M/4$ , the results are not so accurate as with the monobasic acids.

The results obtained for the salts of the bivalent metals show great irregularities, probably on account of the complex ions which are present. For example, the molecular lowering obtained for barium chloride was 24.6 and for barium nitrate 32.8, from which the two values 14.2 and 8.0 are obtained for the modulus of barium. Similar varying results can be obtained from the figures given by Coppet and Müller (*Compt. rend.*, 1902, **34**, 1208) for the lowerings shown by the halogen salts of barium and calcium.

TABLE VI.

	Molecular lowering.		Modulus.
Barium bromide .....	25.14	26.28	10.9
Barium iodide .....	29.24	29.42	11.7
Calcium chloride .....	18.0	18.3	7.8
Calcium bromide .....	20.12	20.93	5.7
Calcium iodide.....	26.09	26.63	8.7

It will be seen at once that there is no regularity comparable with the case of the univalent metals.

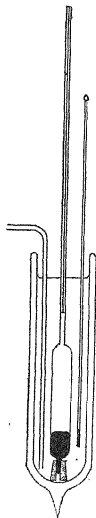
#### EXPERIMENTAL.

The apparatus employed is shown in the diagram; it consists of a dilatometer with a capacity of about 50 c.c. and fitted with a stem 25 cm. long and of 0.5 mm. bore. To compensate for the change in volume with temperature, a portion of the bulb is filled with mercury; the fraction of the total dilatometer volume thus filled is equal to the ratio between the coefficients of cubical expansion of glass and mercury, so that, on a change of temperature, the expansion or contraction of the metal exactly compensates the expansion or contraction of the bulb, the volume of the latter unoccupied by the mercury thus remaining constant.

The dilatometer is filled by means of a tap funnel and a vacuum



pump. The stem of the dilatometer passes through a rubber cork fitted into the opening of the tap funnel which contains the liquid to be introduced into the dilatometer. The funnel and the attached dilatometer is now inverted and connexion made between it and a filter pump. As the pressure is lowered, the air in the dilatometer bulb bubbles through the liquid in the funnel, and on detaching from the pump, the liquid is forced into the dilatometer by the action of the atmospheric pressure. A second and a third exhaustion are usually necessary, and the last trace of air in the bulb is removed by heating. The dilatometer, with the funnel still attached, is now placed in a vacuum-jacketed vessel filled with brine at about  $5^{\circ}$ , and allowed to cool. When the apparatus has attained the temperature of the surrounding liquid, it is disconnected from the tap funnel and a few shavings of ice are added to the liquid in the vacuum flask; air is then driven through the cooling mixture, so as to stir it until the ice has melted. The apparatus is now left for a quarter of an hour to allow the dilatometer to assume the temperature of the bath; this temperature is then noted, and the level of the liquid in the dilatometer tube measured; the apparatus is again left, and readings are taken at five-minute intervals until the liquid in the dilatometer ceases to contract; this precaution is necessary in order to ensure that the whole apparatus is in a state of thermal equilibrium. A further small quantity of ice is now added so as to lower the temperature a fraction of a degree, and the process repeated. After several additions of ice, the liquid in the dilatometer reaches its point of maximum density, and on further cooling it expands. As this point is approached, the coefficient of expansion of the liquid diminishes, so that it is difficult to determine the exact temperature of maximum density, and the readings given are only accurate to within about  $0.2^{\circ}$ .



After a measurement, the instrument is warmed so as to expel a little of the contents, and is then inverted so that the mercury runs out. This mercury is dried and reserved for the next determination, whilst the rest of the contents of the dilatometer are removed by means of the filter pump. The instrument is then rinsed with the next liquid to be investigated, and, after the re-

introduction of the mercury, it is filled with the solution and the measurement made as before.

A few other points may be noted. The coefficient of expansion of the glass was calculated between the ordinary temperature and  $100^{\circ}$  by filling the instrument with mercury and weighing the quantity expelled when heated in a steam-jacket, whilst the volume of the bulb was measured by filling with water and weighing at a known temperature. The stem of the instrument was not graduated, but the level of the liquid below the upper end was determined by means of a depth gauge fitted with a vernier; by this means, a change of level of 0.1 mm. could be detected, and, moreover, the labour of regraduation of the stem after an accident was avoided.

#### *Conclusions.*

(1) The lowering of the temperature of the maximum density of water produced by the addition of a solute is directly proportional to the concentration of the latter (law of Despretz).

(2) The lowering produced by a highly ionised binary electrolyte is composed of two separate, independent effects, one due to the acid radicle and the other due to the basic radicle of the electrolyte.

(3) The lowering produced by a highly ionised binary electrolyte of molecular concentration can therefore be calculated by the addition of two moduli to the lowering produced by a molecular solution of a chosen standard substance. The chosen standard was *N*-hydrochloric acid, which gives a lowering of 5.2.

(4) The acid salts of the dibasic acids behave normally, but the neutral salts of such acids and the salts of the bivalent metals do not follow any simple rule in their effect on the temperature of the maximum density.

(5) Feebly ionised organic acids show abnormal effects, but the highly ionised salts derived from them behave in the normal manner.

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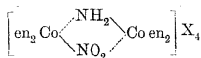
[Received, December 21st, 1918.]

XIV.—*Polar and Non-polar Valency.*

By RAJENDRALAL DE.

In a paper recently published, Briggs (T., 1917, 111, 267) asks: "What is the valency of cobalt in chloropentammine cobaltic chloride,  $(\text{Co}^{\text{5NH}_3}_{\text{Cl}})\text{Cl}_2$ ?" This question has suggested the view set forth in the present paper.

From the study of the optical properties of the tetraethylenediammine- $\mu$ -aminonitrodicobaltic salts,



Werner (*Ber.*, 1913, 46, 3674) concludes that there is no essential difference between the principal and auxiliary valency bonds. Evidently this conclusion may be applicable only to the bonds within the complex radicle (that is, bonds employed in uniting radicles co-ordinated with the cobalt atom). The bonds outside the complex radicle are employed in combining radicles which exist as ions. Their nature is thus entirely different from that of the former ones. A distinction ought therefore to be maintained between the bonds outside the complex radicle and those within it.

We can find an explanation of the valency outside the complex radicle, which is polar in type, from Sir J. J. Thomson's theory of valency. To understand the mechanism of it, let us picture the structure of an atom derived by Thomson. According to him, the atom consists of corpuscles moving in a sphere of uniform positive electrification, and its valency depends on the ease with which corpuscles can escape from, or be received by, the atom. Difficulties, however, arise in explaining the valencies within the complex radicle in the above manner, they being non-polar in type.

During the disintegration of radioactive substances, the negative charges of electricity are carried by  $\beta$ -rays and the positive charges by  $\alpha$ -rays. The  $\beta$ -rays consist of expelled particles—not atoms of matter, but free atoms of negative electricity or "electrons." An  $\alpha$ -particle, however, consists of two atomic charges of positive electricity combined with a helium atom—a substance inert in the chemical sense. It may therefore be assumed that the positive electricity can have an attraction for the mass itself, even if there be no charge of negative electricity on it. Thomson ("Rays of Positive Electricity and their Application to Chemical Analysis," p. 40) also observes that molecules with positive charges are quite

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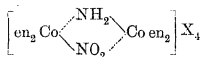
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common, whilst those with negative charges of electricity are very rare. This property which the positive electricity possesses affords an explanation of the phenomena of the valencies inside the complex radicle of a complex salt.

In order to explain the phenomena of the above valencies, we shall consider Rutherford's view as regards the constitution of an atom. According to him, a positive nucleus is situated in the centre, whilst electrons move around it in various concentric rings. We shall conceive this nucleus as having a binding capacity for the radicles which are co-ordinated with a metallic atom in the case of complex salts. It is significant that no positive radicles, such as ammonium, tetramethylammonium, etc., which can exist as cations, have been observed to combine with a metallic atom forming a complex radicle. Negative radicles, such as Cl (chloro-),  $\text{NO}_2$  (nitro-), etc., however, do form a complex radicle with a metallic atom. These negative radicles also carry negative charges of electricity when they exist as anions.

Let us form a picture of the mechanism as conceived above. We have the positive nucleus of the metallic atom (capable of forming a complex radicle) in the centre, and around it there are various concentric rings along which the electrons move. We may assume that adjacent to the outermost ring of electrons constituting the atomic structure there are the neutral molecules, for example,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , etc., or the negative radicles, for example, Cl,  $\text{NO}_2$ , etc., or both these neutral and negative radicles, held by the influence of the positive nucleus of the metallic atom concerned.

Accordingly, in the case of tetraethylenediammine- $\mu$ -aminonitrodicobaltic salts, radicles within the complex radicle may be supposed to be attached to the positive nuclei of its cobalt atoms, and thereby, the valencies within the complex radicle being taken to be all alike, the two cobalt atoms become linked to the two groups in the middle, namely,  $\text{NO}_2$  and  $\text{NH}_2$ , in a similar way.

The conditions favourable to the formation of complex salts may now be stated. The number of concentric rings in the structure of an atom grows large as the atomic weight increases, and, thereby, the structure also becomes more complex. According to Rutherford, however (Soddy, "The Chemistry of the Radio-elements," 1914, Part II, p. 39), the mass of an atom is concentrated in an exceedingly small central nucleus. Hence, with the decrease in the atomic volume, only the rings will decrease in size, and the outermost ring will approach nearer to the nucleus. We have already supposed the radicles, co-ordinated with a metallic atom, to be placed adjacent to its outermost ring of electrons and also bound by its nucleus. Evidently, the attraction of the nucleus

for the mass of the radicles would increase where there are possibilities of their being placed near to the nucleus, that is to say, where the atomic volume is small. In fact, metals that are capable of forming complex salts, as, for example, chromium, iron, manganese, cobalt, nickel, copper, ruthenium, rhodium, palladium, osmium, iridium, platinum, gold, etc., are situated on the troughs of Lothar Meyer's atomic volume curve. Here it may also be mentioned that Ephraim (*Ber.*, 1912, **45**, 1322; 1913, **46**, 3103; 1914, **47**, 1828; *Zeitsch. physikal. Chem.*, 1913, **81**, 513, 539; **83**, 196), from his study of the strength of the auxiliary valencies of various metals, has drawn the conclusion that the strength of the auxiliary valencies falls with the increase of the atomic volume of the metal concerned. We thus find a further support for the above assumption.

It will be observed that the metals which form complex salts are mostly found both in the "ous" and the "ic" state of their ionic condition, as, for instance, we have Cr<sup>++</sup> (chromous), Cr<sup>+++</sup> (chromic), Co<sup>++</sup> (cobaltous), Co<sup>+++</sup> (cobaltic), etc. It may also possibly be that the "ous" condition of the metallic ion is more favourable to the formation of a complex radicle. During the reduction of a metallic ion from the "ic" to the "ous" state, there is an alteration in the electric charge of its rings, and the probability is that this alteration is confined to the outermost ring (Soddy, *ibid.*). Evidently, in the "ous" condition of the metallic atom, there is a less number of electrons in its outermost ring. Keeping in view the structure of an atom, it would be natural to expect that, ordinarily, the outer rings of electrons would offer themselves as a shield against the attraction of the positive nucleus for the radicles which may be co-ordinated with a metallic atom. The case is, however, different in its "ous" state, for, there being produced a weakness in the shield, due to a less number of electrons in the ring, the attraction of the nucleus will obtain an opportunity of manifesting itself by forming a complex radicle. It is known that chromic chloride has to be reduced to the chromous state for the preparation of chrom-ammonia salts (Christensen, *J. pr. Chem.*, 1881, [ii], **23**, 54). Similarly, in the preparation of cobalt-ammonia and platinum-ammonia compounds (Gerhardt, *Annalen*, 1850, **76**, 307), the starting materials are the "ous" salts of the metal concerned.

Lastly, it is found that the formation of a complex anion is a more general phenomenon than the formation of a complex cation; for example, there are compounds of the type  $[M(C_2O_4)_3]R_3$ , where M may be Vd, Cr, Mn, Fe, Co, Rh, Al, As, Sb, or Bi (Werner, "New Ideas on Inorganic Chemistry," p. 115, ed. 1911). It

seems possible that there is a connexion between the increase of attraction of a metallic atom for these negative radicles (co-ordinated with it) and the cause which occasions the presence of negative charges of electricity on them when they exist as anions.

We have already supposed that the valencies outside the complex radicle are caused by electrons of the outermost ring constituting the atomic structure. These electrons may therefore be termed *valence-electrons*. Obviously, the number of the valence-electrons of a metallic atom corresponds with that of its maximum valencies outside the complex radicle. In the case of the complex metal-ammonia compounds, this maximum valency is exhibited when all the radicles co-ordinated with the metallic atom are  $\text{NH}_3$  or  $\text{H}_2\text{O}$ , and when a negative radicle is introduced into the above complex radicle the number of valencies outside the complex one is decreased (that is, the number of valence-electrons appears to become less). We may call those valence-electrons which seem to have vanished in this way *bound valence-electrons*, and those which have caused the appearance of valencies outside the complex radicle *free valence-electrons*. We may also notice that the maximum number of free valence-electrons (that is, electrons which can escape from a metallic atom, forming a complex cation) is the same as the maximum number of electrons which can be received by the atom in addition to its own valence-electrons, when it forms a part of a complex anion. For illustrating this point, we may cite the compounds: (i)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ , where the complex radicle is a tervalent cation, (ii)  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ , where the complex radicle is a tervalent anion, and (iii)  $[(\text{NH}_3)_3\text{Co}(\text{NO}_2)_3]$ , a non-electrolyte. In the third compound, no electron has escaped or been received by the metallic atom, but all the three valence-electrons, along with the three univalent negative radicles, have been bound by its positive nucleus. Regarding the question at hand, namely, that of the number of valencies in chloropentamminecobaltic chloride, it may be said that here the cobalt atom contains three valence-electrons—one is bound along with the univalent chloro-radicle co-ordinated with cobalt, and the remaining two have caused the appearance of valencies of polar type outside the complex radicle. Besides these three valence-electrons, the metallic atom possesses six valency bonds of non-polar type caused by the attraction of its positive nucleus.

The structure of the complex radicle as conceived above explains also the phenomenon of the directional nature of the auxiliary valency bonds, indicated by the stereoisomeric compounds of complex metal-ammonia salts, for the nucleus, being centrally placed in the structure of an atom (metal), has an advantage in exerting



its attraction along different directions, which the electrons moving in their orbits cannot possibly have. The assumption of the nuclear attraction, however, need not be confined to these cases of complex derivatives alone. The phenomena of non-polar valency may, in general, be considered to have arisen from this attraction.

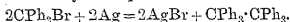
The kind of valency exhibited in organic compounds is a typical non-polar one. If we compare the valencies of the carbon atom with those of metallic ones, employed in co-ordinating radicles with them, we find that both these two kinds are non-polar and directional in nature (shown by the stereoisomerides of the carbon compounds and those of complex metal-ammonia derivatives). This similarity in their character may indicate the probability of their being brought about by the same cause, namely, by the attraction of the positive nucleus of an atom. The assumption receives further support from the small atomic volume of carbon (as shown in Lothar Meyer's atomic volume curve). It has already been supposed that the attraction of the nucleus for radicles should increase as the atomic volume decreases, and this should tend to a maximum when the volume becomes very small.

Nernst is of opinion that the forces by which the carbon atoms in a crystal of diamond are held together are identical with the attraction of its four valencies called into play in the formation of organic compounds, that is to say, "the forces of cohesion are identical in nature with the forces of chemical affinity" ("The Theory of Solid State," p. 6). The cohesive forces are found to increase with the decrease of the atomic volume of elements. They may therefore arise from the very same nuclear attraction of atoms mentioned before. An inspection of the behaviour of carbon and its compounds might help in giving some light in this direction.

In the process of the synthesis of diamond, an immense pressure is brought about by the contraction of iron in which carbon has been dissolved. Evidently, for effecting union (that is, saturation of the valencies of carbon atoms), the atoms are required to be brought very near to one another. It may also be noted that in the case of the carbides of metals, the carbides  $\text{Li}_2\text{C}_2$ ,  $\text{CaC}_2$ , etc., where the metals are of large atomic volumes, are decomposed by water, whilst the carbides  $\text{Cr}_3\text{C}_2$ ,  $\text{Cr}_4\text{C}$ , etc., where the metals in combination are placed on a trough in the atomic volume curve (that is, are of small atomic volumes), form stable compounds. Taking into consideration that the mass of an atom is concentrated in an exceedingly small central nucleus in the structure, it seems possible that carbon atoms would exert only a very feeble attraction when placed a little apart or when combined with metals of large atomic volumes. The various rings of electrons around the

nucleus, which have already been compared to shields, may also occasion a further hindrance in their union.

Further light will be thrown on the above if the following view is taken of the constitution of triphenylmethyl. It is found that in solution triphenylmethyl has a molecular weight corresponding with the formula  $(CPh_3)_2$  (Gomberg and Cone, *Ber.*, 1904, 37, 2033). This is what may be expected from its mode of preparation:



As the compound is very reactive, even at a low temperature, it has been assumed that it is rather a derivative of tervalent carbon. Exposure to the air, even for a very short time, is sufficient to transform it into a peroxide of the constitution  $CPh_3 \cdot O \cdot O \cdot CPh_3$ .

We may, however, represent the constitution of triphenylmethyl as  $CPh_3 \cdots CPh_3$ . The weak attraction between the two carbon atoms is shown by the dotted line. The feebleness of their attraction may be due to the inability of the carbon atoms to approach very near to each other on account of the hindrance caused by the large phenyl groups attached to them. The hindrance referred to may be of the type similar to that of steric hindrance (Wegscheider, *Monatsh.*, 1895, 16, 148), and their reactivity may be due to the possibility of their drawing small atoms very near to them. Viewing the constitution given for the oxidation product, it is seen that by the intervening of two oxygen atoms the large radicles have been placed apart, and by the union of the two carbon atoms with two oxygen atoms (small indeed compared with the triphenylmethyl radicle) a stable compound has been formed.

According to our assumption, radicles bound by the positive nucleus should not show any polar character. Although the valency of carbon is ordinarily non-polar, there are a few organic compounds where it seems to function as polar, as, for instance, in hydrogen cyanide and in organic acids, where we have the radicles  $\cdot C \equiv N$  or  $\cdot N \equiv C$  and  $R \cdot CO_2 \cdot$  respectively, besides hydron. There are also sodium acetylide,  $CH \equiv CNa$ , silver acetylide,  $C_2Ag_2$ , and cuprous acetylide,  $C_2Cu_2$ , where the hydrogen atoms of acetylene have been displaced by metallic atoms. In order to explain this anomaly, we may consider Sir J. J. Thomson's observation that "when the discharge tube contains such gases as  $CH_4$ ,  $CO_2$ ,  $CO$ , where there are no bonds between two carbon atoms in the molecule, we find negatively charged carbon atoms, but no negatively charged molecules. When, however, we use compounds such as acetylene,  $HC \equiv CH$ , ethylene,  $H_2C \equiv CH_2$ , or ethane,  $H_3C \cdot CH_3$ , where, according to the usual interpretation of the constitution of these substances, there are bonds between carbon atoms in the molecule, then we find molecules as well as atoms of carbon with the negative

charge" (*loc. cit.*). He is also of the opinion that on account of the unsaturated valencies of the carbon atoms in the molecule, it has been possible for the negative corpuscles to become attached to them (*ibid.*). A similar explanation may be applicable in the above cases. In them, more than one bond of carbon has been occupied with the other element combined with it, and a corpuscle received from an adjacent hydrogen atom may become attached to the remaining part of the compound, thus giving rise to their polar character.

Compounds such as  $\text{LiH}$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , etc.,  $\text{Ni}(\text{CO})_4$ ,  $\text{Co}_2(\text{CO})_8$ , etc., and also groups of atoms forming radicles, such as  $\text{CO}_3$ ,  $\text{NO}_3$ ,  $\text{SO}_4$ , etc., being formed by non-polar valencies, may have their origin in the nuclear attraction. We may also ascribe the forces by which atoms and molecules in a crystal are held together to the same attraction. These forces have been supposed to be caused by residual valency, which has also been assumed to bring about the solution of a substance in a solvent (Baly, "Spectroscopy," 1912, p. 487). The phenomena of solution should necessarily be considered to be due to the same attraction of the nucleus. In these cases, the size of the molecules may account for the feeble character of their binding. Lastly, all catalytic substances which are employed in gaseous reactions may be supposed to owe their catalytic action to the positive nuclei of the atoms in them. Indeed, the study of the dissociation of the hydrogen molecule into atoms, and other similar studies, have convinced Langmuir (*J. Amer. Chem. Soc.*, 1916, **38**, 2221) that prior to the dissociation, absorption of hydrogen by tungsten wire, due to its secondary valency, does take place. We see, therefore, that the nuclear attraction plays a great part in all chemical phenomena.

Regarding the number of valencies of the non-polar type for different elements, it may be noted that carbon (placed in the first trough of Lothar Meyer's atomic volume curve) has four valencies, whilst other elements (placed in subsequent troughs of the curve) generally have six. In the case of the complex platinum-ammonium salts, however, the derivatives of the platinous salts, for example,  $[(\text{NH}_3)_4\text{Pt}]\text{Cl}_2$ , tetra-amminoplatinous chloride, show the number of auxiliary (non-polar) valencies to be four, whilst those of the platonic salts, for example,  $[(\text{NH}_3)_6\text{Pt}]\text{Cl}_4$ , hexa-amminoplatinic chloride, the number is six. The increase of two non-polar valencies in the latter case has been attended with an increase of two polar ones. Also the directions of these valencies, in the former case, lie in a plane, whilst in the latter case there are two additional directions lying in the same line perpendicular to the above plane. Whether and how the electrons constituting

the atomic structure influence the number and directions of the non-polar valencies of different elements awaits further study.

My best thanks are due to Prof. P. C. Rây for his kind help and encouragement.

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[Received, October 2nd, 1917.]

### XV.—*The Interaction of Stannous and Arsenious Chlorides.*

By REGINALD GRAHAM DURRANT.

THE action of stannous chloride on arsenious oxide dissolved in hydrochloric acid was first noticed by A. Bettendorf (*Sitzungsber. Niederrhein. Ges. Bonn*, 1869, 128\*) two years after his discovery of yellow arsenic [*ibid.*, 1867, 67, and (full paper) *Annalen*, 1867, **144**, 110].

He records the formation of a voluminous, brown precipitate which proved to be arsenic (96—99 per cent.) with traces of non-removable tin. He showed that the rate of precipitation increases with ascending specific gravity of the arsenious solution. By dissolving magnesium ammonium arsenate in acid he made a standard solution and treated this with stannous chloride in varying dilutions of hydrochloric acid. (His figures will be quoted later on.) From these results he showed that the reaction is extremely delicate. It may be utilised for determining arsenic in sulphuric or crude hydrochloric acid. During a distillation with the latter he observed a faint yellow coloration, which disappeared after a few hours. Arsenic was found to be present in this sample of hydrochloric acid, but he was unable to prove that the fading coloration was due to arsenic.

The observation of this yellow coloration has decided me to record a very remarkable yellow precipitate which, in 1914, I exhibited as "yellow arsenic" to the Science Masters' Association in London. The precipitate was quite bright yellow at first, and was always kept in the dark except when shown for short periods. After a year

\* I am indebted to Dr. Hatchett Jackson who recently procured me a rescript of this paper from the Bodleian Library.

it had become a dull mustard colour, being still in the original, well-corked flask and surrounded by the original solution (a mixture of arsenious and stannous chlorides in nearly normal hydrochloric acid). Every effort was made to repeat this, but in vain. When filtered off, the precipitate appeared very dull and shrunken on the paper. After washing, it was specially tested for sulphur (since arsenious sulphide is yellow), but no trace of sulphur was found. The presence of arsenic was proved.

On many points I find that my observations have been anticipated by Bettendorf, in particular the possibility of making the reaction a means of differentiating arsenic from antimony.

#### EXPERIMENTAL.

##### *The Nature of the Arsenic Precipitated.*

Arsenic is probably in a colloidal state before it is precipitated, for (i) the precipitate invariably contains a trace of tin salts (chloride as well as tin), and this cannot be removed completely by prolonged washing; (ii) two similar solutions (reactants, 0.44*N*- and 3*N*-hydrochloric acid) were left corked for two days and remained quite clear. One was then diluted with an equal volume of water. After four days both had deposited arsenic. A third solution at the start was made up to the lower of the above concentrations and remained perfectly clear for twenty-five days.

The appearance of solid arsenic is always preceded by a pale buff tint; from this a buff-brown precipitate falls, and is best observed from such admixtures as yield a very slow deposit. If this deposit, after washing, is immediately shaken with carbon disulphide, arsenic is found to be dissolved. The yield is rather greater if carbon disulphide is shaken violently with the two chloride solutions while they are interacting. On five occasions small, pale particles were observed to rise from the clear disulphide solution during spontaneous evaporation. They moved about rapidly, congregating in the centre of the surface, then darkened, and finally settled on the bottom of the dish in the form of grey arsenic.

Erdmann (*Zeitsch. anorg. Chem.*, 1902, **32**, 453) obtained arsenic soluble in carbon disulphide by reducing arsenious oxide with zinc dust in the presence of the solvent. Very small quantities were obtained by the author in this way.

These results, and those referred to in the Introduction, indicate that the very earliest deposit of arsenic is of the yellow type, but that unless certain unascertained conditions obtain, the yellow variety spontaneously becomes brown or grey.

*Nature and Conditions of the Reaction.*

The obvious equation is  $2\text{AsCl}_3 + 3\text{SnCl}_2 = 3\text{SnCl}_4 + 2\text{As}$ , and when weights of the reactants, corresponding with this equation, are placed in hydrochloric acid of sufficiently high concentration the action reaches completion in a few hours. With other weights excess of either reactant corresponds with calculation. The action has been proved to be irreversible, for, if finely divided arsenic is boiled with solutions of stannic chloride in the presence of hydrochloric acid of varying concentration, in no case does the resulting solution give any precipitate with mercuric chloride.

A very careful experiment was made in order to ascertain if the anhydrous chlorides react.

Fresh arsenious chloride was so arranged that on movement of the handle of an air-pump some would drop on to dry, powdered stannous chloride—also under the receiver. After four days' final drying with phosphoric oxide, the experiment was made. Beyond the faintest darkening no discoloration occurred. On exposure to air a distinct brown colour overspread the powder, and when a drop of water was added a heavy crusting of arsenic appeared immediately.

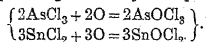
*General Method of Estimating the Rate of Progress of Action.*

Separate solutions containing known weights of the two chlorides were made up in known concentrations of hydrochloric acid. Portions of these solutions were evaluated separately by means of standard permanganate. The results were found to agree with the known concentrations. All stock flasks were re-tested from time to time.

Small dry flasks were placed in a large thermostat, and into these definite volumes of both chloride solutions were introduced by separate pipettes.

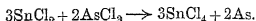
After definite intervals water was added. The dilution effectively stops the action. The contents of each flask were then filtered and uniformly washed. Standard permanganate was used to determine the amounts of stannous and arsenious chlorides remaining in the filtrates and wash-water.

The action of the permanganate may be expressed:



As the filtrates required less permanganate than did the sum of

the separate solutions, the deficit became a measure of the change which had occurred. Two-fifths of this deficit were due to the precipitation of arsenic and the rest to the formation of stannic chloride in the reaction:



*Errors.*—The sources of error in this process are: (1) imperfect washing, (2) loss by adsorption, (3) oxidation of stannous chloride due to access of air.

The two first, considered together, were found to give rise to an error probably less than 2 per cent.

The third source of error was almost eliminated by keeping the stock solutions of stannous chloride in a well-corked flask and by introducing carbon dioxide immediately after use on every occasion. In the same way the reaction took place in small, corked flasks in which the air was displaced by carbon dioxide. Air had access only during the process of filtration.

*Calculations.*—The recognised integration equations for first and second order reactions were applied to a large number of determinations. In no case did the velocity constants conform to the second order. The results quoted are from the first-order equation,  $\frac{1}{t} \log \frac{a}{a-x}$ , where  $a=100$ ,  $x$ =percentage of change, and  $t$ =time in minutes. Hence the mean value of  $k$  for each set of experiments represents a special figure by which the relative speeds may be compared.

TABLE I.

$t=12.5^\circ$ . Normalities:  $\text{SnCl}_2=0.507$ ,  $\text{AsCl}_3=0.584$ ,  $\text{HCl}=6.06$ .

$N/4$ -Permanganate used. Complete oxidation should correspond with a deficit of 45.6 c.c.

Interval, minutes.	Deficit, c.c.	Percentage change.	$k \times 10^4$ .	*
2	3.65	8.0	1.81	
5	9.3	20.8	2.03	
8	16.65	36.5	2.46	
10	17.05	[37.4]	[2.03]	
12	26.25	57.5	3.09	
15	29.4	64.5	3.00	
20	33.85	74.2	2.94	
30	38.45	84.3	2.68	
40	40.1	87.9	2.29	
50	40.8	89.5	2.96	
65	41.9	91.9	[1.68]	
100	42.85	93.9	2.21	
120	43.6	95.6	2.97	
180	43.9	96.3	2.40	

Mean 2.57

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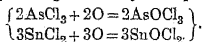
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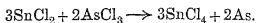
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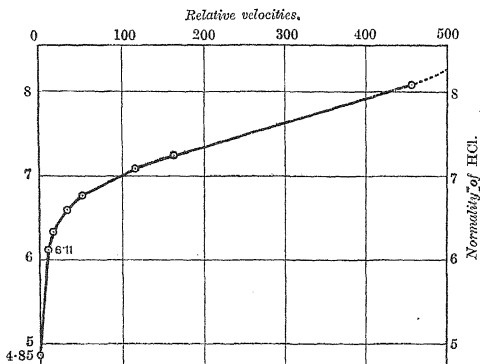
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100	42.85	93.9	2.21
120	43.6	95.6	2.97
180	43.9	96.3	2.40

Mean 2.57

Various further unimolecular values of  $k$  were obtained. These were found to depend more on the concentration of hydrochloric acid than on anything else. The results made it possible to choose suitable concentrations for systematic study.

*Influence of Hydrochloric Acid.*

In the following experiments 0.2500 gram of stannous chloride



Relative velocities of the reaction:  $3\text{SnCl}_2 + 2\text{AsCl}_3 = 3\text{SnCl}_4 + 2\text{As}$ , due to alterations of hydrochloric concentration. See Table II.

Temperature =  $12^\circ$ .

acted on the equivalent weight of arsenious chloride in each case. The concentration of hydrochloric acid alone was varied.

TABLE II.

$t = 12^\circ$ . Reactant Normality = 0.298.

Normality of HCl.	Range of change, per cent.	Mean value, $k \times 10^3$ .
10.09	40—61	21.2
8.10	36—64	13.5
7.25	32—63	4.76
7.09	34—78	3.43
6.77	13—63	1.46
6.60	21—69	0.944
6.34	26—64	0.436
6.11	41—53	0.293
4.85	19—53	0.0293

The curve, obtained by plotting these relative velocities against concentration of hydrochloric acid between  $4.85N$  and  $8.10N$ , is exceedingly regular. Its sharpest curvature is in the neighbourhood of  $6.5N$ . If the regularity persisted up to the limit of possible hydrochloric acid concentration (about  $10.3N$ ) then the velocity at  $10.09N$  would be well over a thousand times what it is at  $4.85N$ —as measured it is only 723 times as great.

*Influence of Simultaneous Change in Concentration of Reactants.*

In all these experiments, the concentration of hydrochloric acid remained constant at  $6N$ .  $t=18.4$ .

Four 250 c.c. flasks— $A$ ,  $B$ ,  $A_1$ ,  $B_1$ —contained, respectively,  $\text{SnCl}_2=1.74N$ ,  $\text{AsCl}_3=1.76N$ ,  $\text{SnCl}_2=0.87N$ ,  $\text{AsCl}_3=0.88N$ .

The concentration of hydrochloric acid became  $6N$  as soon as the mark in each flask was reached.

Equal volumes from  $A$  and  $B$  were mixed in six small flasks, and after 4, 6, 8, 10, 12, and 14 minutes, respectively, their filtrates were titrated with  $N/4$ -permanganate.

In the same way, equal volumes from  $A_1$  and  $B_1$  were treated from seven flasks after 24, 32, 48, 64, 80, 96, and 112 minutes, respectively, the filtrates being titrated with  $N/8$ -permanganate.

In each set, the range of progress was from 30 to 70 per cent.

For  $AB$  set, mean value  $k \times 10^2 = 4.33$ .

For  $A_1B_1$  set, mean value  $k_1 \times 10^2 = 0.557$ .

Hence  $k/k_1 = 7.77$  for the range between 30 and 70 per cent. The range between 30 and 40 per cent., however, gave  $k/k_1 = 5.5$ .

*Effect of altering the Concentration of Each Reactant Separately.*

Preliminary work had appeared to show that arsenious chloride reacts as a second, and stannous chloride as a first power.

The following solutions were prepared, tested, and preserved with all possible care. Five c.c. of stannous chloride solution reacted with 5 c.c. of arsenious chloride solution in each case. The washing was strictly uniform, so that errors hence arising were similar.

The mean results, (2) and (4) in the following table, are fairly concordant. Those of (3) and (5) are more so.

The results from comparison of (1), (4), and (5) confirm the preliminary work with respect to arsenious chloride, which is seen to react as a second power.

The period preceding the first appearance of arsenic, from a solution of its chloride at one-fifth the original concentration, was noticed to be just about twenty-five times as great as it had been.

TABLE III.

HCl = 6*N*.  $t = 16.7^\circ$ .

(1) <i>N</i> -AsCl <sub>3</sub> acting on <i>N</i> -SnCl <sub>2</sub> in 12 minutes required c.c. <i>N</i> /4-KMnO <sub>4</sub>		Required by theory after 33.3 per cent. change.
Mean of 2 readings	27.85	26.66
(2) <i>N</i> -AsCl <sub>3</sub> on <i>N</i> /2-SnCl <sub>2</sub> in 12 minutes	22.3	23.3
(3) <i>N</i> -AsCl <sub>3</sub> " on <i>N</i> /3-SnCl <sub>2</sub> in 12 minutes	20.8	22.2
(4) <i>N</i> -SnCl <sub>2</sub> " on <i>N</i> /2-AsCl <sub>3</sub> in 48 minutes	22.55	23.3
(5) <i>N</i> -SnCl <sub>2</sub> " on <i>N</i> /3-AsCl <sub>3</sub> in 108 minutes	20.9	22.2

This suggested a method of working to a standard tint, as in Nesslerisation; moreover, the method compares the earlier stages of action on which calculations are more appropriately based.

The tint used in table IV was obtained by the action of hydrogen sulphide on a very dilute solution of lead acetate.

TABLE IV.

HCl = 6*N*.  $t = 10^\circ$ .

*Times to reach Standard Tint are given in Seconds.*

Stannous chloride.	Arsenious chloride $f$	$\rightarrow$ <i>N</i> .	$\rightarrow$ <i>N</i> /2.	$\rightarrow$ <i>N</i> /3.	Total.	Ratio.	$\sqrt{c}$ .
<i>N</i>		30	110	260	400	1.0	1.0
<i>N</i> /2		40	160	360	560	1.40	1.41
<i>N</i> /3		50	220	460	730	1.82	1.73
Total		120	490	1080			
Ratio		1	4.08	9			
$1/c^2$		1	4	9			

A similar set of nine readings referred to another artificial standard tint gave ratios: powers of AsCl<sub>3</sub>, 1:4:3:10.0; powers of SnCl<sub>2</sub>, 1:1.37:1.80.

The *N*/3-stannous chloride solution, on testing, was found to have deteriorated slightly; the others had not.

A solution of *N*/4-stannous chloride was made. Using *N*/2-arsenious chloride against *N*/2- and *N*/4-stannous chloride, the times were 230 and 320 seconds respectively, giving a ratio 1/1.39, again closely approaching  $1/\sqrt{2}$ .

The results here given lead to the conclusion that in this reaction *arsenious chloride reacts as a second power and stannous chloride reacts to the power of the square root of its concentration.*

The figure 5.5, noted in the last paragraph for the change between 30 and 40 per cent., is quite consistent with the results here given, since  $2^2 \times \sqrt{2} = 5.64$ .

The action of stannous chloride to the square root of its concentration is also in agreement with Bettendorf's figures (*loc. cit.*, 1869). He took 0.001 gram of arsenic dissolved in 1 c.c. in each of five experiments, adding this to a definite amount of stannous chloride solution in the presence of hydrochloric acid. In the four last experiments he also added 50, 100, 200, and 400 c.c. of hydrochloric acid (presumably of similar concentration).

An immediate precipitate occurred in the first experiment, and the arsenic appeared in 5, 8, 12, and 20 minutes, respectively, in the others.

Neglecting 1 c.c. of arsenious chloride + an unknown volume of stannous chloride solution originally taken, his concentrations were 1:2:4:8, his times were 1:1.6:2.4:4, figures which approach 1:1.41:2:2.83, but exceed them in each case, because of the influence of the second power action of arsenious chloride, present in very small relative amount. (His experiments were made to show the delicacy as regards arsenic.)

#### *Effect of Dilution with Water.*

The stock solutions, when mixed, were at concentrations  $\text{HCl} = 6N$  and reactants each at  $0.88N$ . When undiluted, this mixture produced 70 per cent. change in twelve minutes. The dilutions (in ten steps) finally brought all the concentrations to one-third of the above.

The hydrochloric acid normalities, and the state of change after five days are noted in each case.  $t = 16^\circ$ .  $6N$ ,  $5.45N$ , and  $5N$  had reached complete change.  $4.61N$  89 per cent.,  $4.29N$  59 per cent.,  $4N$  24.4 per cent.,  $3.75N$  14.2 per cent.,  $3.53N$  5.6 per cent.,  $3.3N$  3 per cent.,  $3N$  1 per cent., and  $2N$  no change and no subsequent sign of action after 29 days. This retarding action was made use of in all previous experiments when titrations with permanganate were made, the dilution with water being sufficient to reduce the concentration to one-third or less.

#### *Summary.*

(1) There is evidence that arsenic in process of precipitation is partly soluble in carbon disulphide. In certain circumstances, arsenic may appear as a yellow deposit.

(2) The anhydrous chlorides (arsenious and stannous) do not interact.

(3) Acceleration of the action is caused chiefly by increase in the concentration of hydrochloric acid, next by that of arsenious chloride, and least of all by that of stannous chloride. Arsenious chloride acts as a second power and stannous chloride to the power of the square root of its concentration.

### Conclusions.

The various phenomena and the figures given can be accounted for on the hypothesis that this action is between chloride ions, arsenious ions, and the stannous complex  $H_2SnCl_4$ .

Stoppage by dilution must be due to the destruction of arsenious ions by hydrolytic action.

(1) Chloride ions proceed partly from arsenious chloride and partly from hydrochloric acid, and they act as a first power.

The velocity constants found in table II are thus explained.

HCl normality.	$k \times 10^3$ .	$k/k$ .	$Cl'/Cl$ .
10.09	21.2	1.57	7.09
8.10	13.5	2.83	3.55
7.25	4.76	1.37	1.54
7.09	3.43	2.35	2.08
6.77	1.46	1.54	1.58
6.60	0.944	2.16	1.88
6.34	0.436	3.22	2.66
6.11	0.293	10.00	5.28
4.85	0.0293		
Aggregate		25.04	25.66

In the last column, the numerator gives the sum of chloride ions due to arsenious chloride and those due to increased hydrochloric acid concentration; the denominator is constant, and represents the chloride ions due to the 0.298*N*-arsenious chloride, which is constant throughout the table. In the lower portion of the table, the arsenious chloride is not wholly ionised; in the upper portion, hydrochloric acid becomes less ionised at its higher concentrations. As is seen, the aggregate acceleration is directly proportional to the increase of chloride concentration.

(2) Positively charged arsenious ions also act as a first power. Arsenious chloride as a whole appears, therefore, to act as a second power.

(3) That a compound of hydrochloric acid and stannous chloride exists in solution was indicated by Young (*J. Amer. Chem. Soc.*, 1901, 23, 21, 450), and several stannochlorides, corresponding with

the formula  $M_3SnCl_4$ , have recently been described (compare Druce, *Chem. News*, 1918, 117, 193). In the reaction, this complex must be decomposed in order to produce stannic chloride, and this decomposition may account for the complex acting to the power of the square root of its concentration.

According to accepted theory, the order of a reaction is governed by the slowest reactant. The order here is unimolecular, and the slowest reactant is this complex. Essentially the action consists in the disintegration of the complex by circumambient ions.

THE COLLEGE,  
MARLBOROUGH.

[Received, July 30th, 1918.]

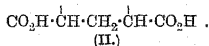
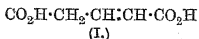
## XVI.—*Experiments on the Elimination of the Carboethoxyl Group from Tautomeric Systems. Part I. Derivatives of Indene.*

By CHRISTOPHER KELK INGOLD and JOCELYN FIELD THORPE.

THERE have been placed on record within recent years (T., 1905, 87, 1669, 1685; 1911, 99, 2187, and subsequent papers of the same series) a number of experiments dealing with substances possessing the kind of tautomerism which is associated with the three-carbon system



These experiments have for the most part dealt with glutaconic acid and its alkyl derivatives, and the conclusion was reached that glutaconic acid itself has the symmetrical or "normal" structure (II), the unsaturated or "labile" form (I) being too unstable to have any but a momentary existence.

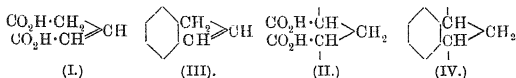


When, however, alkyl groups were introduced into the three-carbon system, the unsaturated form was found to become very noticeably more stable with increasing weight of the substituents.

It was thought desirable to extend these investigations to substances possessing the three-carbon tautomeric complex, but containing groups other than carboxyl attached to its terminal carbon atoms—preferably to some substance in which the possible

symmetry of the molecule could be tested without in any way tampering with the three-carbon system.

Such a substance presents itself in the hydrocarbon indene, the analogy of which to glutaconic acid becomes apparent when the formulæ are written together, thus:



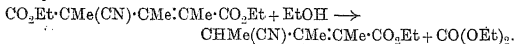
It was hoped originally that the accuracy either of III or of IV might be proved by preparing solid substituted indenenes from  $\alpha$ -hydrindones of the types V and VI.



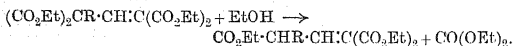
If the unsubstituted three-carbon system of the indene nucleus is symmetrical, as would be expected from analogy to unsubstituted glutaconic acid, the ketones V and VI should yield the same indene, whilst, if unsymmetrical, two different indenenes should result.

We have not yet been able to elaborate methods leading to the preparation of suitable ketones of the types V and VI in sufficiently large quantities to ensure the success of this method of attack. In the meantime, however, we have made use of more easily available materials to obtain evidence bearing on the subject, and in particular to investigate a reaction which has been repeatedly observed among esters of the glutaconic series, and appears to be peculiar to tautomeric compounds.

In 1905 the observation was made (Rogerson and Thorpe, T., 1905, 87, 1703) that ethyl  $\gamma$ -cyano- $\alpha\beta\gamma$ -trimethylglutaconate readily passed into ethyl carbonate and ethyl  $\gamma$ -cyano- $\alpha\beta\gamma$ -trimethylcrotonate under the influence of cold sodium ethoxide:

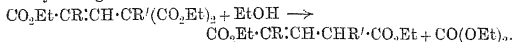


Since that time, fairly extensive use has been made of this reaction in the preparation of a series of alkylated glutaconic esters (Thole and Thorpe, T., 1911, 99, 2187). Thus the monoalkylated products derived from Conrad and Guthzeit's yellow sodium compound (*Annalen*, 1883, 222, 259) yielded ethyl carbonate along with tribasic esters:



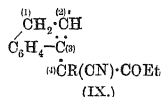
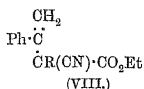
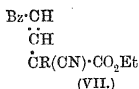


The tribasic esters did not decompose when treated with excess of the same reagent, but on further alkylation gave  $\alpha\gamma$ -dialkyl derivatives, which reacted readily to form ethyl carbonate and dialkylated glutaconic esters:



The study of these and similar cases led to a generalisation regarding the determining cause of these reactions. They have always been found to be peculiar, in substances of the glutaconic type, to those in which all the terminal hydrogen atoms of the three-carbon system have been substituted. It was therefore inferred that the tendency in such cases to acquire the hydrogen atom necessary to enable the substance to pass into its tautomeric form is such that a carbethoxyl group readily becomes detached from the molecule and replaced by an atom of hydrogen under the influence of a suitable reagent. We shall have occasion more than once to make use of this general rule.

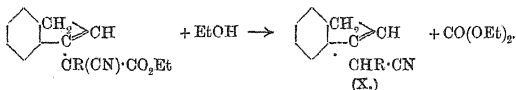
The ethyl carbonate reaction is therefore very closely bound up with the tautomerism of the three-carbon system. One would not therefore expect derivatives of vinylacetic acid, such as those represented by formulæ VII and VIII, in which the double bond would be purely static, to exhibit this reaction to any marked degree.



It was therefore decided to prepare an ester of the type IX and investigate its behaviour towards cold sodium ethoxide. The similarity with VII and VIII is clear. If the double bond in the ester IX really possesses the same stable character, we should for similar reasons expect it to be unreactive. This conclusion is in agreement with the generalisation above cited; for if the three-carbon system (1), (2), (3) (see formula IX) in the indene ring is non-tautomeric and the double bond quite static between the carbon atoms (2) and (3), then, since this same double bond enters also into the three-carbon system (2), (3), (4), the latter must be non-tautomeric as well. Its normal form would clearly be incapable of existence, since the central carbon atom (3) is rendered permanently quaternary by the double bond. In such an ester we should not, in view of the above-mentioned generalisation, expect to find any tendency to acquire an atom of hydrogen, which,

if it were acquired, could not possibly be mobile. If, on the contrary, we found that an ester of the type IX actually did possess a noteworthy tendency to acquire a hydrogen atom in place of its carbethoxyl group, we should have to look on the fact as evidence of the tautomeric or dynamic character of the three-carbon system (1), (2), (3) of the indene ring. This follows by simply reversing the argument.

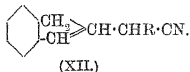
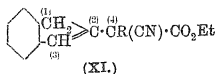
Actually, we have succeeded in preparing a number of indenyl 3-cyanoacetic esters of the type IX, and have found that the lower members of the series possess a very marked tendency to lose their carbethoxyl group as ethyl carbonate when treated with quite a small quantity of sodium ethoxide at 30°. The ester in which R=Me, for example, when treated with as little as one-sixth of a molecule of sodium ethoxide, reacts at 30° in the course of a few minutes. The yield of the decarbethoxylated nitrile is 60 per cent., the remainder of the material passing into an insoluble substance of high molecular weight. In all the cases of this reaction investigated, there was a greater or less quantity of insoluble by-product formed along with the nitrile X and ethyl carbonate.



With homologous alkyl derivatives (R=Et and R=Pr<sup>n</sup>), the reaction becomes successively more sluggish, and an increased quantity of by-product is formed, the yield of nitrile consequently diminishing. This is quite analogous to all that has been observed in regard to the same reaction when applied to the glutaconic esters (T., 1911, 99, 2192). Two points, to which no analogy has as yet been investigated or observed among the glutaconic esters, require, however, special notice. The ester for which R=allyl was found to be very much more reactive than the corresponding *n*-propyl derivative. Its reactivity was quite of a similar order to that of the methylated ester. The other point is that a branched chain in the alkyl group appears to inhibit the reaction practically altogether. Thus the esters for which R was *isopropyl*, *isobutyl*, and *isoamyl* gave no nitrile after remaining for twenty-four hours with one-sixth of a molecular proportion of sodium ethoxide at 30°.

In order to obtain a comparative check on these results, we decided to investigate an indenyl-2-cyanoacetic ester of the type XI. This clearly differs from IX only in the fact that in XI the

cyanoacetic residue is attached to the central carbon atom of the indene system. Now if the double bond in XI is entirely static as regards possible interchange across the system (1), (2), (3), then the carbon atom (4) will be the terminal carbon atom of one three-carbon system only, namely, the system (3), (2), (4).



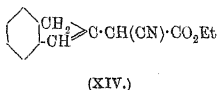
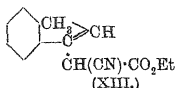
It should therefore differ but little in reactivity from the carbon atom (4) in the corresponding ester of type IX. If, on the other hand, the system (1), (2), (3) of XI possesses a mobile hydrogen atom and a mobile double bond, it is clear that a hydrogen atom attached to the carbon atom (4) will have a double possibility of "wandering"; it might wander either to (1) or to (3). We might, therefore, in view of the general rule, expect to find an ester of the type XI even more prone than the corresponding ester of the type IX to exchange its carbethoxyl group for an atom of hydrogen.

Experiment shows the latter supposition to be amply justified. The ester prepared was that for which  $R=Me$ . With one-twentieth molecular proportion of sodium ethoxide, there was obtained after three minutes at  $15^\circ$  a practically quantitative yield of the corresponding nitrile (XII:  $R=Me$ ).

This connexion between the ease of elimination of the carbethoxyl group and the potential mobility of the hydrogen attached to the carbon of the cyanoacetic residue suggests a possible explanation of the broad facts both in the indene and glutaconic series in regard to the effect of the size of an alkyl group on the ease of the reaction. It seems likely to be connected with the fact that when heavier alkyl groups were introduced into the glutaconic molecule, they were found to increase the stability of the unsaturated form, and consequently to reduce the predominance of the normal and the potential mobility of the tautomeric hydrogen atom (since tautomerism depends on the possibility of the existence of the normal form). An ester in which the degree of tautomerism of the three-carbon system has been so reduced by the entrance of a large alkyl group would, in view of the generalisation, be expected to exhibit a smaller tendency to acquire an atom of hydrogen, and this is what is actually found to be the case.

In complete accord with the great ease with which the ester XI exchanges its carbethoxyl group for an atom of hydrogen, and with the presumed excessive mobility of the latter, is the behaviour of the unmethylated ester XIV. The esters IX and XI were

obtained by alkylating the esters XIII and XIV respectively. These esters differ in acidity in the sense that, as one would expect from the different reactivities of their alkyl derivatives, the cyanoacetic hydrogen atom of indenyl-2-cyanoacetic ester (XIV) is more loosely attached than that of the corresponding indenyl-3-derivative (XIII). Thus ethyl indenyl-2-cyanoacetate is a weak acid

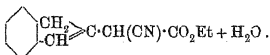
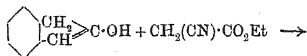
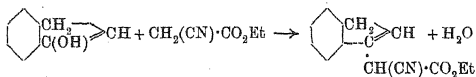


forming a sodium salt which is not hydrolysed in aqueous solution, being decomposed only by slightly acid substances, such as carbonic acid. Ethyl indenyl-3-cyanoacetate, on the other hand, only forms a sodium salt in complete absence of water.

It is perhaps worth noticing that when either of the indenylcyanoacetic esters (XIII and XIV) are converted into or liberated from their salts, a deep crimson colour is immediately developed. This fades in the course of a few seconds, both the free esters and the solid salts being colourless.

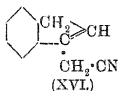
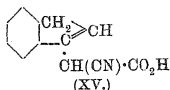
Another colour change which was regularly observed in the course of these experiments took place when the alkylated esters (IX and XI) were treated with sodium ethoxide. An indigo-blue colour immediately developed, and gradually faded as the elimination of the carbethoxyl group proceeded.

The preparation of the indenylcyanoacetic esters (XIII and XIV) was readily accomplished by condensing  $\alpha$ -hydrindone or  $\beta$ -hydrindone with ethyl cyanoacetate in the presence of piperidine or diethylamine:



When ethyl indenyl-3-cyanoacetate was hydrolysed either by acid or by alkali, the cyano-acid (XV) was formed, although not without considerable decomposition. This acid on heating above its melting point gave off carbon dioxide, and from the dark-

coloured residue indenyl-3-acetonitrile (XVI) was isolated by



vacuum distillation. This is the first member of the series of homologous nitriles of which X is the type. It cannot, of course, be prepared directly from the cyano-ester (XIII) by the action of sodium ethoxide, for reasons already indicated.

Neither the compound, XVI, nor any of its homologues appears to form a sodium compound when treated with alcoholic sodium ethoxide, and all attempts to introduce another alkyl group into these compounds, using sodium or potassium ethoxide and an alkyl iodide, met with failure. The same was the case when the methylated nitrile, XII, derived from  $\beta$ -hydrindone, was used.

#### EXPERIMENTAL.

The  $\alpha$ -hydrindone required for these experiments was prepared from  $\beta$ -phenylpropionic acid by a method essentially the same as that described by Kipping (T., 1894, 65, 680), but with the introduction of certain modifications which so improved the yield as to make this substance far more easily available than it has hitherto been.

*$\beta$ -Phenylpropionyl Chloride.*—It was found advantageous to use thionyl chloride in the preparation of this substance instead of phosphorus pentachloride.  $\beta$ -Phenylpropionic acid (100 grams) was mixed with an equal weight of thionyl chloride in a flask fitted with an efficient condenser. The reaction was started by gentle heat and allowed to proceed for one and a-half to two hours, when the evolution of gas had ceased. The contents of the flask were then transferred to a Claisen distillation flask and heated at 100°/25 mm. until all the thionyl chloride had distilled over. The residue was then fractionated under 22.5 mm. pressure, and 110 grams boiling at 121–122° were collected. The theoretical yield is 112 grams.

*$\alpha$ -Hydrindone.*—Pure  $\beta$ -phenylpropionyl chloride being thus available, it was found possible to carry out the internal condensation, whereby hydrogen chloride is eliminated and  $\alpha$ -hydrindone produced, with much better results than Kipping was able to obtain with the impure chloride at his disposal. Whilst he seldom obtained more than a 56 per cent. yield, it was found that with the pure chloride a yield of 75 per cent. was always secured. The

reaction with the pure chloride is far more violent than with the impure product, and hence the mixture must be heated for a few minutes only. With this exception, the details given by Kipping were closely followed.

*$\beta$ -Hydrindone.*—The  $\beta$ -hydrindone required for these experiments was prepared by the improved modification (P., 1911, 27, 108) of the original process described by Moore and Thorpe (T., 1908, 93, 165).

*Condensation of  $\alpha$ -Hydrindone with Ethyl Cyanoacetate in the Presence of Secondary Bases: Ethyl Indenyl-3-cyanoacetate (XIII, p. 148).*

Since  $\alpha$ -hydrindone readily dissolves in ethyl cyanoacetate, it is not necessary to use any solvent in this condensation. A solution of 19 grams of the ketone in 16 grams of the ester was treated with 6.5 grams of diethylamine and the mixture allowed to remain at 40° for twenty-four hours. At the end of that time, the tube, which contained a stiff paste of crystals of the condensation product, was cooled for an hour at 0°, and the crystals were drained on porous porcelain. The compound separates from alcohol in colourless, needle-shaped crystals melting at 104°; it is moderately soluble in dry ether and readily so in benzene, chloroform, or acetone. The yield represents about 55 per cent. of the theoretical, and is but little affected when piperidine is used in place of diethylamine:

0.1031 gave 0.2805 CO<sub>2</sub> and 0.0538 H<sub>2</sub>O. C=74.20; H=5.80.

0.2492 „ 13.8 c.c. N<sub>2</sub> at 19° and 742.6 mm. N=6.19.

C<sub>14</sub>H<sub>13</sub>O<sub>2</sub>N requires C=74.0; H=5.7; N=6.2 per cent.

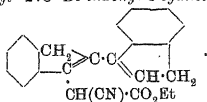
The ester reacts with alcoholic sodium ethoxide, forming a sodium compound, from which the ester is regenerated by the action of water. There is no doubt but that this sodium compound contains the metal attached to the cyanoacetic residue, and that therefore the ester described above has the constitution assigned to it. When alcoholic sodium ethoxide was added to the ester, a deep crimson colour was invariably formed. This faded after a few seconds to a bright yellow, which persisted so long as the solution remained alkaline.

*Condensation of  $\alpha$ -Hydrindone with Ethyl Cyanoacetate in the Presence of Alcoholic Sodium Ethoxide.*

The condensation with sodium ethoxide appears to be of a considerably more complex character than when secondary bases are used. Thus, when an alcoholic solution of  $\alpha$ -hydrindone is added

to a hot suspension in alcohol of the sodium compound of ethyl cyanoacetate, there is formed a mixture of substances which may be precipitated by adding water. This mixture consists chiefly of two compounds, melting at  $143^{\circ}$  and  $88-89^{\circ}$  respectively, which may be separated and obtained in a state of purity by fractional crystallisation, first from alcohol and finally from a mixture of absolute alcohol and benzene. The former compound was identified with anhydrobis- $\alpha$ -hydrindone (Found: C=87.74; H=5.70. Calc.: C=87.8; H=5.7 per cent.), which is recorded as melting at  $142-143^{\circ}$  (Kipping, T., 1894, 65, 495).

*Ethyl 2:3'-Di-indenyl-3-cyanoacetate,*



The substance melting at  $88-89^{\circ}$  may be made to become the principal product if the order in which the condensing substances are mixed is reversed. 3.3 Grams of  $\alpha$ -hydrindone were dissolved in a small quantity of hot alcohol, and a hot solution of 0.6 gram of sodium and 2.8 grams of ethyl cyanoacetate in 15 grams of alcohol was slowly added. A few minutes after the addition was complete, the solution was rapidly cooled and poured into water. Hydrochloric acid was then added, and the oily precipitate extracted with ether, the extract washed with dilute sodium carbonate solution and with water, and then dried. The solid residue obtained on evaporation of the ether, when recrystallised from alcohol, weighed 0.8 gram:

0.1545 gave 0.4575  $\text{CO}_2$  and 0.0790  $\text{H}_2\text{O}$ . C=80.78; H=5.68.

0.1818 „ 6.7 c.c.  $\text{N}_2$  at  $17^{\circ}$  and 766.1 mm. N=4.23.

$\text{C}_{23}\text{H}_{19}\text{O}_2\text{N}$  requires C=80.9; H=5.6; N=4.1 per cent.

*Ethyl 2:3'-di-indenyl-3-cyanoacetate* separates from the usual solvents in pinkish-buff needles melting at  $88-89^{\circ}$ . It is oxidised instantly by cold alkaline permanganate. With alcoholic sodium ethoxide, it forms a yellow sodium compound, from which the original ester can be regenerated.

*Hydrolysis of Ethyl Indenyl-3-cyanoacetate: Indenyl-3-cyanoacetic Acid* (XV, p. 149).

The hydrolysis of the ester melting at  $104^{\circ}$  is a matter of some difficulty, owing to the ease with which it undergoes deep-seated

decomposition with acids and alkalis. Thus, on boiling with acids (dilute hydrochloric or sulphuric), only a 6 per cent. yield of the acid is obtained. The acid can be produced in 36 per cent. yield by alkaline hydrolysis, but only by working within very narrow limits. Four grams of the ester were treated with 8 c.c. of 4*N*-sodium hydroxide, and the mixture was heated as rapidly as possible to the boiling point and maintained there for twenty seconds with vigorous shaking. The oil dissolved, forming a clear red solution, which was kept boiling for thirty seconds longer and then rapidly cooled. The crystalline sodium salt which separated was collected, dissolved in water, and the solution, after passing through a wet filter, acidified with hydrochloric acid. The acid separated as a white precipitate, which crystallised from alcohol in small prisms melting and decomposing at about 200°, the melting point depending on the rate of heating. The point of instantaneous decomposition as measured by the Maquenne block is 237°. The acid is sparingly soluble in water or dry ether:

0.1251 gave 0.3326 CO<sub>2</sub> and 0.0509 H<sub>2</sub>O. C=72.51; H=4.52.

0.2164 „ 13.8 c.c. N<sub>2</sub> at 19° and 755 mm. N=7.24.

C<sub>12</sub>H<sub>9</sub>O<sub>2</sub>N requires C=72.4; H=4.5; N=7.1 per cent.

#### *Indenyl-3-acetonitrile (XVI, p. 149).*

The pure, recrystallised acid (4.4 grams) was heated at 250° until the evolution of carbon dioxide had ceased. The dark-coloured oil which remained was then distilled under diminished pressure and the colourless distillate cooled in ice. The solid residue, which melted below the ordinary temperature, was recrystallised from light petroleum below 0°, and obtained in long, colourless needles melting at 18°:

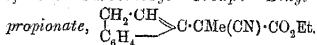
0.0820 gave 0.2568 CO<sub>2</sub> and 0.0426 H<sub>2</sub>O. C=85.41; H=5.77.

0.1430 „ 11.3 c.c. N<sub>2</sub> at 19° and 761.2 mm. N=9.06.

C<sub>11</sub>H<sub>9</sub>N requires C=85.2; H=5.8; N=9.0 per cent.

The attempts which were made to alkylate this nitrile did not meet with any success, and we were quite unable to find the conditions by which the nitrile could be hydrolysed to the corresponding acid.

#### *Alkylation of Ethyl Indenyl-3-cyanoacetate and the Elimination of the Carbethoxyl Group: Ethyl α-Indenyl-3-α-cyano-*



In order to prepare this substance, 12 grams of the ester melt-

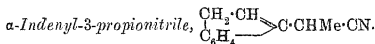


ing at 104° were dissolved in the least possible quantity of alcohol at 70° and added to a solution of 1.2 grams of sodium in 16 grams of alcohol. Ten grams of methyl iodide were then added, and the mixture was heated until the yellow colour had entirely disappeared and the solution had become neutral, an operation which usually required ten minutes. The addition of water precipitated an oil which, when extracted by ether, yielded a solid residue after the solvent had been evaporated. The compound crystallises from a mixture of light petroleum and ether in large cubes melting at 60°; it is readily soluble in the usual organic solvents, excepting light petroleum. The yield was 70 per cent. of the theoretical:

0.1418 gave 0.3900 CO<sub>2</sub> and 0.0816 H<sub>2</sub>O. C=74.96; H=6.39.

0.2818 „ 14.4 c.c. N<sub>2</sub> at 19° and 783 mm. N=5.92.

C<sub>15</sub>H<sub>15</sub>O<sub>2</sub>N requires C=74.7; H=6.2; N=5.8 per cent.



Six grams of the carboxylic ester were dissolved in cold alcohol and an alcoholic solution containing 0.1 gram of sodium was added. The solution was kept at 30° for a short time, when the blue colour which had developed was discharged, and the liquid had a strong odour of ethyl carbonate. The liquid was poured through a filter, water was added, and the precipitate which was formed was induced to solidify by shaking. It was then collected, dried, and extracted with hot light petroleum, the nitrile being deposited from the solvent, on cooling, in long, colourless needles melting at 118°. It may also be recrystallised from dilute alcohol. The yield is 60 per cent. of the theoretical:

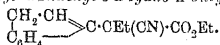
0.1032 gave 0.3227 CO<sub>2</sub> and 0.0603 H<sub>2</sub>O. C=85.28; H=6.49.

0.2118 „ 15.4 c.c. N<sub>2</sub> at 23° and 771 mm. N=8.30.

C<sub>12</sub>H<sub>11</sub>N requires C=85.2; H=6.5; N=8.3 per cent.

The nitrile could not be hydrolysed, and all attempts to introduce another alkyl group into it were without success.

*Ethyl α-Indenyl-3-α-cyano-n-butyrate,*

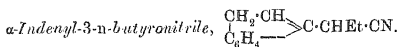


This ester was prepared in the same way as the methyl derivative already described. It is a colourless oil which boils at 200°/25 mm.:

0.1304 gave 0.3604 CO<sub>2</sub> and 0.0785 H<sub>2</sub>O. C=75.38; H=6.69.

0.2363 „ 11.6 c.c. N<sub>2</sub> at 22° and 768 mm. N=5.62.

C<sub>16</sub>H<sub>17</sub>O<sub>2</sub>N requires C=75.3; H=6.7; N=5.5 per cent.



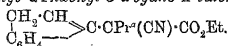
This nitrile was produced from the carboxylic ester by the action of a small quantity of alcoholic sodium ethoxide under the same conditions as those which were described for the methyl derivative. The crude solid precipitated by water was extracted with hot alcohol, and the nitrile obtained from the alcoholic extract by the addition of water. It crystallises from light petroleum in long needles melting at  $76^\circ$ . The yield is 20 per cent. of the theoretical:

0.1306 gave 0.4067  $\text{CO}_2$  and 0.0835  $\text{H}_2\text{O}$ .  $\text{C}=84.93$ ;  $\text{H}=7.11$ .

0.1882 „ 12.6 c.c.  $\text{N}_2$  at  $23^\circ$  and 771 mm.  $\text{N}=7.64$ .

$\text{C}_{13}\text{H}_{13}\text{N}$  requires  $\text{C}=85.2$ ;  $\text{H}=7.1$ ;  $\text{N}=7.7$  per cent.

*Ethyl  $\alpha$ -Indenyl-3- $\alpha$ -cyano- $n$ -valerate,*

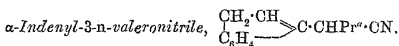


This ester was produced by the action of  $n$ -propyl iodide on the sodium compound of ethyl indenyl-3-cyanoacetate in alcoholic solution. The reaction was complete after heating for forty-five minutes, and the product was then isolated in the usual way. The ester is an oil which boils at  $210^\circ/20$  mm.:

0.1259 gave 0.3502  $\text{CO}_2$  and 0.0797  $\text{H}_2\text{O}$ .  $\text{C}=75.86$ ;  $\text{H}=7.03$ .

0.2169 „ 10.0 c.c.  $\text{N}_2$  at  $22^\circ$  and 768 mm.  $\text{N}=5.26$ .

$\text{C}_{17}\text{H}_{19}\text{O}_2\text{N}$  requires  $\text{C}=75.8$ ;  $\text{H}=7.1$ ;  $\text{N}=5.2$  per cent.



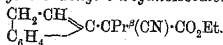
This compound was prepared in the same manner as the ethyl derivative, although in the present instance the reaction proceeded much less readily. It was isolated in the usual way and crystallised from light petroleum in colourless needles melting at  $67^\circ$ . The yield was only 10 per cent. of the theoretical:

0.1028 gave 0.3210  $\text{CO}_2$  and 0.0710  $\text{H}_2\text{O}$ .  $\text{C}=85.16$ ;  $\text{H}=7.68$ .

0.2018 „ 12.8 c.c.  $\text{N}_2$  at  $23^\circ$  and 768 mm.  $\text{N}=7.20$ .

$\text{C}_{14}\text{H}_{15}\text{N}$  requires  $\text{C}=85.3$ ;  $\text{H}=7.6$ ;  $\text{N}=7.1$  per cent.

*Ethyl  $\alpha$ -Indenyl-3- $\alpha$ -cyanoisovalerate,*



*iso*Propyl iodide was found to react with the sodium compound

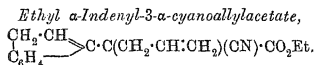
of ethyl indenyl-3-cyanoacetate in the same manner as *n*-propyl iodide, and the product was isolated in the same way. In this case, the ester was obtained as a colourless oil which boiled at 260°/120 mm., and solidified in the receiver. The solid crystallised from light petroleum in colourless prisms melting at 72°. The yield represented 60 per cent. of the theoretical:

0.1115 gave 0.3105 CO<sub>2</sub> and 0.0716 H<sub>2</sub>O. C=75.95; H=7.15.

0.1859 „ 8.6 c.c. N<sub>2</sub> at 22° and 768 mm. N=5.28.

C<sub>17</sub>H<sub>19</sub>O<sub>2</sub>N requires C=75.8; H=7.1; N=5.2 per cent.

This ester was scarcely changed by alcoholic sodium ethoxide under the experimental conditions which caused the other esters to lose their carbethoxyl groups as ethyl carbonate. Most of the original ester and a small amount of insoluble matter were recovered.

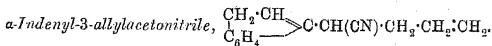


Allyl iodide reacted with the sodium compound of ethyl indenyl-3-cyanoacetate in boiling alcoholic solution in the course of a few seconds. The product was isolated in the usual way and crystallised from light petroleum containing a little dry ether in nearly cubical crystals melting at 65°. The yield was 65 per cent. of the theoretical:

0.1240 gave 0.3484 CO<sub>2</sub> and 0.0715 H<sub>2</sub>O. C=76.63; H=6.41.

0.2954 „ 13.6 c.c. N<sub>2</sub> at 19° and 764 mm. N=5.31.

C<sub>17</sub>H<sub>17</sub>O<sub>2</sub>N requires C=76.4; H=6.4; N=5.2 per cent.

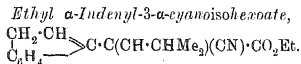


The action of a trace of alcoholic sodium ethoxide on the ester caused the carbethoxyl group to be eliminated, and gave a yield of 40 per cent. of the corresponding nitrile, the same conditions being employed as those described in the former experiments. The nitrile crystallises from light petroleum in colourless needles melting at 108°:

0.1064 gave 0.3366 CO<sub>2</sub> and 0.0647 H<sub>2</sub>O. C=86.28; H=6.75.

0.2732 „ 17.6 c.c. N<sub>2</sub> at 23° and 768 mm. N=7.31.

C<sub>14</sub>H<sub>12</sub>N requires C=86.2; H=6.7; N=7.1 per cent.



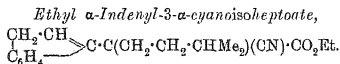
This ester was prepared in the usual manner from *isobutyl* iodide and ethyl indenyl-3-cyanoacetate. It distilled at 260°/40 mm. as a pale yellow oil:

0.1956 gave 0.5481 CO<sub>2</sub> and 0.1290 H<sub>2</sub>O. C=76.43; H=7.33.

0.2600 „ 11.6 c.c. N<sub>2</sub> at 22° and 761 mm. N=5.07.

C<sub>18</sub>H<sub>21</sub>O<sub>2</sub>N requires C=76.3; H=7.4; N=4.9 per cent.

Like the *isopropyl* derivative, this ester did not lose its carbethoxyl group by treatment with cold sodium ethoxide. After being submitted to the same experimental conditions as the other esters, the recovered material gave, on analysis, C=76.89, H=7.56, N=5.13, indicating that it was practically unchanged. (The de-carbethoxylated compound, C<sub>15</sub>H<sub>17</sub>N, requires C=85.3; H=8.1; N=6.6 per cent.)



When prepared from the ester melting at 104°, and *isoamyl* iodide, and isolated in the usual way, this ester distilled at 270°/34 mm. as an almost colourless oil:

0.1680 gave 0.4749 CO<sub>2</sub> and 0.1173 H<sub>2</sub>O. C=77.08; H=7.76.

0.2127 „ 9.0 c.c. N<sub>2</sub> at 22° and 766 mm. N=4.80.

C<sub>19</sub>H<sub>23</sub>O<sub>2</sub>N requires C=76.8; H=7.7; N=4.7 per cent.

The carbethoxyl group could not be eliminated under the customary experimental conditions. The material recovered from the solution of sodium ethoxide gave, on analysis, C=77.31, H=7.92, N=4.95, indicating that it consisted of the unchanged compound (C<sub>16</sub>H<sub>19</sub>N, the carbethoxyl-free compound, requires C=85.3, H=8.5, N=6.2 per cent.).

*Condensation of β-Hydrindone with Ethyl Cyanoacetate in the Presence of Secondary Bases.*

When a mixture of β-hydrindone and ethyl cyanoacetate is treated with a secondary base such as piperidine or diethylamine, there is generally formed a mixture of two crystalline compounds melting at 116° and 176° respectively. The latter contained no nitrogen and gave, on analysis, C=87.62, H=5.81 (C<sub>18</sub>H<sub>14</sub>O requires C=87.8; H=5.7 per cent.). It is therefore probably

identical with anhydrobis- $\beta$ -hydrindone, the melting point of which is given as approximately  $170^{\circ}$  (Heusler and Schieffer, *Ber.*, 1899, 32, 32). The amount of bis-compound formed varies very much with the conditions, and unless the condensation is kept well under control it may become the sole product.

*Ethyl Indenyl-2-cyanoacetate* (XIV, p. 148).

By exercising care, it was found possible to obtain a solid product containing as much as 65 per cent. of ethyl indenyl-2-cyanoacetate and 35 per cent. of anhydrobis- $\beta$ -hydrindone. Ten grams of  $\beta$ -hydrindone were dissolved in 9 grams of ethyl cyanoacetate, and the solution was cooled below  $18^{\circ}$  while 30 drops of diethylamine were added. After the addition of each drop, the solution was immediately shaken and well cooled in running water. After completing the addition of the base, the tube containing the mixture was immersed in cold water for thirty minutes, when it was withdrawn and allowed to remain at the ordinary temperature for forty-eight hours. At the end of that time the stiff paste of crystals which filled the tube was spread on porous porcelain and allowed to remain until colourless. The crude solid mixture of condensation products, which usually weighed about 13 grams, was rubbed to a fine powder under a little dry ether and roughly separated by extracting with four times its weight of boiling 95 per cent. alcohol, the bulk of the bis-compound being left undissolved. The crude ester deposited by the filtrate melted between  $90^{\circ}$  and  $110^{\circ}$ . It was finely powdered and stirred into an excess of 4*N*-sodium hydroxide at  $30^{\circ}$ , the whole diluted with an equal bulk of water, quickly filtered, and treated with aqueous sodium hydrogen carbonate in excess. The precipitated ester was caused to solidify by shaking, and then collected and triturated with water. After draining and recrystallising from alcohol, it was obtained in long, colourless needles melting at  $116^{\circ}$ :

0.1261 gave 0.3417  $\text{CO}_2$  and 0.0646  $\text{H}_2\text{O}$ .  $\text{C}=73.91$ ;  $\text{H}=5.70$ .

0.1834 „ 9.7 c.c.  $\text{N}_2$  at  $16^{\circ}$  and 772.5 mm.  $\text{N}=6.25$ .

$\text{C}_{14}\text{H}_{13}\text{O}_2\text{N}$  requires  $\text{C}=74.0$ ;  $\text{H}=5.7$ ;  $\text{N}=6.2$  per cent.

The compound is very readily soluble in hot alcohol, but sparingly so in cold. It is also very readily soluble in cold benzene, chloroform, or acetone, and sparingly so in ether or light petroleum. It tends to form coloured products when its alkaline solution is exposed to the air, and the yield obtained by the sodium hydroxide separation therefore depends greatly on the speed with which the operations are carried out.

The separation was also effected by means of a long series of fractional distillations.

tional crystallisations from alcohol. The ester obtained by both methods proved to be the same substance, showing that the formation of a sodium salt had not involved any isomeric change, and that the compound must therefore have the structure assigned to it.

The ester is readily soluble in 4*N*-sodium hydroxide, and is not reprecipitated when a large bulk of water is added. It is insoluble, however, in sodium carbonate, and is therefore precipitated from the hydroxide solution by carbon dioxide or a bicarbonate. During the precipitation by either of these reagents or by an acid, a transient, red colour always appeared. A similar transient colour was invariably observed when an alcoholic solution of the ester was treated with aqueous or alcoholic potassium hydroxide or alcoholic sodium ethoxide.

*Sodium Derivative.*—One gram of the ester was dissolved in twice the theoretical quantity of 4*N*-sodium hydroxide at 50°. On cooling, a colourless, crystalline sodium derivative separated out. The alkaline liquid was poured off from the crystals, which were then washed with ice-water and dried in a vacuum over phosphoric oxide:

0.3002 gave 0.0860  $\text{Na}_2\text{SO}_4$ .  $\text{Na} = 9.28$ .

$\text{C}_{14}\text{H}_{12}\text{O}_2\text{NNa}$  requires  $\text{Na} = 9.24$  per cent.

When kept in a closed space, the sodium compound slowly decomposes, acquiring a green colour, but if spread in a thin layer over a large area in a dry atmosphere it can be kept for several weeks. Although the compound itself is colourless, its solution in water is orange. This solution on acidification becomes deep red for a few moments, the colour quickly fading as the free ester separates out.

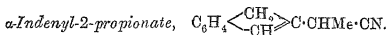
*Methylation of Ethyl Indenyl-2-cyanoacetate and the Elimination of the Carbethoxyl Group: Ethyl  $\alpha$ -Indenyl-2- $\alpha$ -cyano-*  
*propionate,  $\text{C}_8\text{H}_4\left\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CH} \end{smallmatrix}\right\rangle\text{C}\cdot\text{CMe}(\text{CN})\cdot\text{CO}_2\text{Et}$ .*

The methylation of ethyl indenyl-2-cyanoacetate was accomplished both by the action of methyl iodide on the dry sodium compound suspended in alcohol and by the more usual process of treating the free ester with alcoholic sodium ethoxide and methyl iodide. The ester was precipitated with water and extracted with ether. After washing the extract with water and drying, the ether was evaporated and the residual oil crystallised from light petroleum containing a trace of ether. The ester separated in dense, colourless prisms melting at 56°. The yield was about 70 per cent. of the theoretical:

0.1035 gave 0.2837 CO<sub>2</sub> and 0.0580 H<sub>2</sub>O. C=74.23; H=6.22.

0.1653 „ 8.4 c.c. N<sub>2</sub> at 18° and 779 mm. N=5.90.

C<sub>15</sub>H<sub>15</sub>O<sub>2</sub>N requires C=74.7; H=6.2; N=5.8 per cent.



The elimination of the carbethoxyl group of ethyl indenyl-2-cyanopropionate was found to proceed with great ease in the presence of a small quantity of sodium ethoxide. Thus with one-twentieth of a molecular proportion of sodium at 15°, the reaction was complete in about three minutes. On adding water, the nitrile separated out. After allowing the suspension to remain for twenty-four hours, it was filtered, and the solid dried and recrystallised from light petroleum, from which it separated in long, colourless needles melting at 92°:

0.1011 gave 0.3167 CO<sub>2</sub> and 0.0591 H<sub>2</sub>O. C=85.43; H=6.49.

0.1179 „ 8.5 c.c. N<sub>2</sub> at 20° and 764 mm. N=8.22.

C<sub>12</sub>H<sub>11</sub>N requires C=85.2; H=6.5; N=8.3 per cent.

The yield was practically quantitative.

All attempts to hydrolyse this nitrile resulted in deep-seated decompositions taking place, and we were unable to isolate the corresponding acid. Several attempts also were made to introduce another methyl group into the molecule, but without success.

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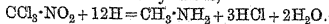
SOUTH KENSINGTON,

[Received, December 6th, 1918.]

## XVII.—The Preparation of Monomethylamine from Chloropicrin.

By PERCY FARADAY FRANKLAND, FREDERICK CHALLENGER, and  
NOEL ALBERT NICHOLLS.

THE products of the reduction of chloropicrin seem to vary with the nature of the reducing agent. With stannous chloride and hydrochloric acid, cyanogen chloride is produced (Raschig, *Ber.*, 1885, 18, 3326). The occasional formation of traces of ammonia was noticed by this chemist, but as a rule, after removing the tin by means of hydrogen sulphide, the product was found to be free from ammonium chloride and the hydrochlorides of hydroxylamine and methylamine. Iron filings and acetic acid (Geisse, *Annalen*, 1859, 109, 282) or tin and hydrochloric acid (Wallach, *ibid.*, 1877, 184, 51) give rise to monomethylamine,



Since chloropicrin may easily be obtained in large quantities, it appeared desirable more closely to investigate its reduction, owing to the importance of monomethylamine in synthetic organic chemistry. It would be inferred from Geisse's paper that the base he obtained was free from ammonia, whilst Wallach states that his product was comparatively very pure and the yield good.

By employing fine iron filings and hydrochloric acid, we have found that the composition of the reduction product depends on the conditions of the experiment. The use of iron and hydrochloric acid in the theoretical quantities (six atomic proportions of iron and nine molecular proportions of acid to one of chloropicrin) in such a way as to prevent the formation of ferrous or ferric hydroxides gave a product rich in ammonium chloride. If chloropicrin is shaken with iron filings and water, the mixture becomes extremely hot and a vigorous reaction sets in, which, however, gradually slackens if no acid is added. By adopting the method employed in the reduction of aromatic nitro-compounds or of nitromethane and nitroethane (Krause, *Chem. Zeit.*, 1916, **40**, 810), the reaction proceeds satisfactorily in the presence of only about one-fortieth of the theoretical amount of hydrochloric acid, and a practically theoretical yield of methylamine hydrochloride is obtained. This usually contains about 4 per cent. of ammonium chloride, but in some of our experiments the quantity of this impurity has been still further reduced. The best results have been obtained by slowly adding the chloropicrin to a well-stirred mixture of iron filings and acidified water. The gradual addition of iron filings to a mixture of acidified water and chloropicrin did not seem to be very satisfactory, so far as could be seen from the few experiments made in this direction. Some reductions carried out by gradually adding chloropicrin to boiling alkaline ferrous hydroxide failed to confirm the results of Geisse (*loc. cit.*), who states that by this method no ammonia is produced. We obtained a product containing about 20 per cent. of ammonium chloride.

The details of a typical large-scale experiment may be briefly outlined. Five hundred grams of fine iron filings were gradually shaken into a large earthenware jar containing 2500 c.c. of water and 60 c.c. of concentrated hydrochloric acid. In this way, the filings were thoroughly moistened and the tendency to clogging was diminished. The jar was fitted with a stirrer and placed in a little cold water; 250 grams of chloropicrin were then gradually added in the course of one-and-a-quarter hours. Too rapid addition of the chloropicrin caused the mixture to froth over. Owing to the large amount of hydrated oxide of iron produced, the stirring was as efficient as possible, otherwise chloropicrin escaped reaction through being enclosed in masses of iron filings or oxide.



The temperature rose considerably, and was maintained at about  $50^{\circ}$ , when the odour of chloropicrin was found to have disappeared after about three hours. The mixture was then gradually added to a boiling solution of sodium hydroxide contained in a large iron can, into which steam was blown. The methylamine was absorbed in hydrochloric acid, the solution evaporated, and the residue dried at  $110^{\circ}$  until constant weight was attained. The crude, dry hydrochloride was obtained in this way in a yield of 95.5 per cent., and contained 53.1 per cent. of chlorine, corresponding with an ammonium chloride content of only 3.5 per cent.

That ammonium chloride is actually produced during the reduction of chloropicrin was shown by treating cold concentrated aqueous solutions of the crude hydrochlorides with gaseous hydrogen chloride. The precipitated solid was collected, carefully freed from adhering hydrochloric acid, and analysed, when it was found to be almost pure ammonium chloride. The analyses of the crude methylamine hydrochloride were checked in some instances by an estimation of the platinum in the platinichloride. The hydrochlorides were evaporated with an excess of chloroplatinic acid solution, and the dry residue was extracted with absolute alcohol, whereby only platinum tetrachloride is removed. The possibility of a partial separation of the platinichlorides of the two bases would thus appear to be excluded.

#### *Summary of Results.*

*Section A.*—In the following experiments, the quantity of acid was very small, and the amount of iron theoretically required for the liberation of 12 atomic proportions of hydrogen (supposing sufficient acid had been present) was employed. The temperature was usually allowed to rise to about  $50$ — $70^{\circ}$ .

Experiment.	1.	2.	3.	4.	5.	6.
Chloropicrin, grams	500	250	250	25	25	25
Iron, grams	1000	500	500	50	50	50
Water, c.c.	3500	2500	2500	200	200	200
Hydrochloric acid, c.c.	100	60	60	12	32	10
Crude hydrochloride, grams	190	98	94	9.5	10.0	9.5
Theoretical weight, grams	205	102.5	102.5	10.2	10.2	10.2
Cl in crude hydrochloride	53.3	53.1	53.6	52.9	52.8	53.1
Hence percentage $\text{NH}_4\text{Cl}$	5.0	3.5	7.0	2.0	1.5	3.5
Pt in crude platinichloride	41.53	41.43	—	—	—	41.33
Hence percentage $\text{NH}_4\text{Cl}$	6.5	2.75	—	—	—	1.10

$\text{NH}_4\text{Cl}$  requires  $\text{Cl} = 66.5$ .  $(\text{NH}_4)_2\text{PtCl}_6$  requires  $\text{Pt} = 43.96$ .

$\text{CH}_3\cdot\text{NH}_2\text{Cl}$  requires  $\text{Cl} = 52.6$ .  $(\text{CH}_3\cdot\text{NH}_2)_2\text{PtCl}_6$  requires  $\text{Pt} = 41.36$  per cent.

*Section B.*—In the experiments described in this section, the quantity of acid employed was much larger (up to 9 molecular proportions, not including the three formed during the reduction), and the iron as in *A*. The chloropicrin and the acid were both added gradually to the iron filings. The percentage of ammonium chloride is seen to have increased considerably.

Experiment.	1.	2.	3.
Chloropicrin, grams.....	25	25	50
Iron, grams .....	50	50	100
Water, c.c. ....	100	50	100
Hydrochloric acid, c.c. ....	200	150	300
Yield of dry hydrochloride, grams .....	9	6.5	15.0
Theoretical weight, grams .....	10.2	10.2	20.5
Cl in crude hydrochloride .....	58.0	60.9	60.5
Hence percentage $\text{NH}_4\text{Cl}$ .....	40.0	60.0	60.0

*Section C.*—In these experiments, the chloropicrin was gradually added to a boiling alkaline ferrous sulphate solution. A considerable amount of ammonia was formed.

*Experiment I.*—Chloropicrin, 25 grams; ferrous sulphate, 550 grams; sodium hydroxide, 300 grams; water, 1800 c.c.

Dry hydrochloride, 7 grams. Theory, 10.2.

Analysis in samples of about 0.2 and 0.1 gram: Cl=56.0, 55.2. Mean=55.6, whence  $\text{NH}_4\text{Cl}$ =22 per cent.

*Experiment II.*—Quantities as in above.

Dry hydrochloride, 9 grams.

Analyses in samples of about 0.5 gram: Cl=54.8, 54.8, 54.6. Mean=54.7, whence  $\text{NH}_4\text{Cl}$ =15 per cent.

#### *Interaction of Methylamine and 1:2:4-Trinitrobenzene.*

With 1:2:4-trinitrobenzene, the alcoholic solution of the base gave an almost immediate deposit consisting of yellow needles melting at 175—176°, and at 176° after one crystallisation. The formation of 2:4-dinitromethylaniline (m. p. 176—177°) by this method does not seem to have been described.

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[Received, January 20th, 1919.]

XVIII.—*The Alkaloids of Holarrhena congolensis, Stapf.*

By FRANK LEE PYMAN.

FRÈRE JUST. GILLET, S.J., a missionary in the Belgian Congo, reported some years ago that, on chewing the leaves of *Holarrhena congolensis*, Stapf, a local anæsthetic effect was produced on the mucous membrane of the mouth. This led the author to examine the alkaloids of the plant in 1913, when a new base, termed *holarrhenine*,  $C_{24}H_{38}ON_2$ , was isolated, together with the alkaloid *conessine*, which has been obtained previously by several authors from other species of *Holarrhena*. The physiological action of *conessine* and *holarrhenine* was studied by J. H. Burn (*J. Pharmacol.*, 1915, 6, 305), who found that whilst they had a local anæsthetic action, this property was of no practical value, since they produced local necrosis when injected subcutaneously.

Since it is improbable that the author will continue this investigation, it is desired to put on record the properties of *holarrhenine* and also the results of a few experiments on *conessine* carried out at that time. These are for the most part in agreement with the recent work of Giemsa and Halberkann (*Arch. Pharm.*, 1918, 256, 201), and confirm the formula  $C_{24}H_{40}N_2$  supported by these authors, not that— $C_{23}H_{38}N_2$ —put forward by Ulrici (*Arch. Pharm.*, 1918, 256, 57). Giemsa and Halberkann's view, that *conessine* contains two dialkylamino-groups, is not shared by the present author, who found *conessine* to contain only three alkyl groups (no doubt methyl groups) attached to the nitrogen atom. Moreover, Polstorff and Schirmer (*Ber.*, 1886, 19, 84) showed that *conessine* dimetho-hydroxide yields, on heating, a crystalline base, together with "ammonia" (doubtless trimethylamine). It is therefore probable that *conessine* contains an *N*-methyl group forming a link in a heterocyclic ring, to which a side-chain bearing a dimethylamino-group is attached. *Holarrhenine* resembles *conessine* in containing three *N*-alkyl groups. It yields a *monoacetyl* derivative,  $C_{26}H_{40}O_2N_2$ , which is diacidic, whence it follows that *holarrhenine* contains a hydroxyl group.

## EXPERIMENTAL.

*Isolation of the Alkaloids.*

Twenty-nine kilograms of the bark of the trunk of *Holarrhena congolensis*, Stapf, were percolated with very dilute hydrochloric

*Section B.*—In the experiments described in this section, the quantity of acid employed was much larger (up to 9 molecular proportions, not including the three formed during the reduction), and the iron as in *A*. The chloropicrin and the acid were both added gradually to the iron filings. The percentage of ammonium chloride is seen to have increased considerably.

Experiment.	1.	2.	3.
Chloropicrin, grams.....	25	25	50
Iron, grams .....	50	50	100
Water, c.c. ....	100	50	100
Hydrochloric acid, c.c. ....	200	150	300
Yield of dry hydrochloride, grams .....	9	6.5	15.0
Theoretical weight, grams .....	10.2	10.2	20.5
Cl in crude hydrochloride .....	58.0	60.9	60.5
Hence percentage $\text{NH}_4\text{Cl}$ .....	40.0	60.0	60.0

*Section C.*—In these experiments, the chloropicrin was gradually added to a boiling alkaline ferrous sulphate solution. A considerable amount of ammonia was formed.

*Experiment I.*—Chloropicrin, 25 grams; ferrous sulphate, 550 grams; sodium hydroxide, 300 grams; water, 1800 c.c.

Dry hydrochloride, 7 grams. Theory, 10.2.

Analysis in samples of about 0.2 and 0.1 gram: Cl=56.0, 55.2. Mean=55.6, whence  $\text{NH}_4\text{Cl}$ =22 per cent.

*Experiment II.*—Quantities as in above.

Dry hydrochloride, 9 grams.

Analyses in samples of about 0.5 gram: Cl=54.8, 54.8, 54.6. Mean=54.7, whence  $\text{NH}_4\text{Cl}$ =15 per cent.

#### *Interaction of Methylamine and 1:2:4-Trinitrobenzene.*

With 1:2:4-trinitrobenzene, the alcoholic solution of the base gave an almost immediate deposit consisting of yellow needles melting at 175–176°, and at 176° after one crystallisation. The formation of 2:4-dinitromethylaniline (m. p. 176–177°) by this method does not seem to have been described.

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XVIII.—*The Alkaloids of Holarrhena congolensis, Stapf.*

By FRANK LEE PYMAN.

FRÈRE JUST. GILLET, S.J., a missionary in the Belgian Congo, reported some years ago that, on chewing the leaves of *Holarrhena congolensis*, Stapf, a local anæsthetic effect was produced on the mucous membrane of the mouth. This led the author to examine the alkaloids of the plant in 1913, when a new base, termed *holarrhenine*,  $C_{24}H_{38}ON_2$ , was isolated, together with the alkaloid *conessine*, which has been obtained previously by several authors from other species of *Holarrhena*. The physiological action of *conessine* and *holarrhenine* was studied by J. H. Burn (*J. Pharmacol.*, 1915, **6**, 305), who found that whilst they had a local anæsthetic action, this property was of no practical value, since they produced local necrosis when injected subcutaneously.

Since it is improbable that the author will continue this investigation, it is desired to put on record the properties of *holarrhenine* and also the results of a few experiments on *conessine* carried out at that time. These are for the most part in agreement with the recent work of Giemsa and Halberkann (*Arch. Pharm.*, 1918, **256**, 201), and confirm the formula  $C_{24}H_{40}N_2$  supported by these authors, not that— $C_{23}H_{38}N_2$ —put forward by Ulrici (*Arch. Pharm.*, 1918, **256**, 57). Giemsa and Halberkann's view, that *conessine* contains two dialkylamino-groups, is not shared by the present author, who found *conessine* to contain only three alkyl groups (no doubt methyl groups) attached to the nitrogen atom. Moreover, Polstorff and Schirmer (*Ber.*, 1886, **19**, 84) showed that *conessine* dimethoxyhydroxide yields, on heating, a crystalline base, together with "ammonia" (doubtless trimethylamine). It is therefore probable that *conessine* contains an *N*-methyl group forming a link in a heterocyclic ring, to which a side-chain bearing a dimethylamino-group is attached. *Holarrhenine* resembles *conessine* in containing three *N*-alkyl groups. It yields a *monoacetyl* derivative,  $C_{26}H_{40}O_2N_2$ , which is diacidic, whence it follows that *holarrhenine* contains a hydroxyl group.

## EXPERIMENTAL.

*Isolation of the Alkaloids.*

Twenty-nine kilograms of the bark of the trunk of *Holarrhena congolensis*, Stapf, were percolated with very dilute hydrochloric

acid. The liquor was made alkaline with ammonia and extracted with chloroform. After distillation of the solvent, the dark, viscous residue was extracted first with light petroleum and then with ether. The light petroleum extract was shaken with dilute hydrochloric acid, the base regenerated with sodium carbonate, and extracted with light petroleum. The extract was distilled, and the residue dissolved in a solution of 0.7 part of hydrated oxalic acid in 4 parts (by weight) of alcohol. On keeping, a colourless, crystalline hydrogen oxalate (m. p.  $249^{\circ}$ ) separated in a yield amounting to 0.9 per cent. of the bark. The oxalate was dissolved in water, the base regenerated by sodium carbonate, and extracted with light petroleum. After distilling the extract, the residue was dissolved in a little acetone and kept, when conessine separated in colourless plates, amounting to 0.25 per cent. of the bark. A further quantity was obtained by working up the mother liquor.

The ethereal extract of the total alkaloids was extracted with dilute hydrochloric acid, and this was basified with ammonia and extracted first with light petroleum and then with ether. The light petroleum extract was worked up as before for conessine. The ethereal extract was concentrated and left for some time, when a small quantity of holarrhenine crystallised out.

#### *Conessine.*

The base employed in this investigation was purified by crystallisation from acetone, which is particularly suitable for the purpose, as Giemsa and Halberkann have remarked. The base is only sparingly soluble in cold acetone, but dissolves in boiling acetone to the extent of approximately 10 per cent. On cooling, it separates in large, colourless plates, which apparently contain acetone of crystallisation, for they effloresce quickly in the air, becoming free from solvent. The base melted at  $125^{\circ}$  (corr.).

Found: C=81.0, 80.7; H=11.3, 11.4; N=7.9; Me(attached to N)=12.5, 13.0.

$C_{24}H_{40}N_2$  requires C=80.8; H=11.3; N=7.9; Me(attached to N)=12.6 per cent.

The molecular weight was determined by the cryoscopic method in benzene:

0.2330 in 29.92 benzene gave  $\Delta t = -0.108^{\circ}$ . M.W.=361.

0.4442 „ 29.92 „ „  $\Delta t = -0.213^{\circ}$ . M.W.=349.

$C_{24}H_{40}N_2$  requires M.W.=356.5.

The specific rotatory power of the base was determined in chloroform solution:

$\alpha_D - 0.28^{\circ}$ ;  $c = 7.268$ ;  $l = 2$  dcm.;  $[\alpha]_D - 1.90^{\circ}$ .

The specific rotatory power of a specimen of the hydrobromide (containing 2.4 per cent. of water) was determined in aqueous solution:

$\alpha_D + 0.56^\circ$ ;  $c = 3.858$ ;  $l = 2$  dcm.;  $[\alpha]_D + 7.4^\circ$  for the anhydrous salt.

*Conessine hydrogen oxalate* forms prisms readily soluble in hot, but rather sparingly so in cold, water, and sparingly soluble in alcohol. It melts and decomposes at  $280^\circ$  (corr.), and is anhydrous.

Found: C = 62.5; H = 8.1.

$C_{24}H_{40}N_2 \cdot 2C_2H_2O_4$  (536.5) requires C = 62.6; H = 8.3 per cent.

*Holarrhenine*,  $C_{24}H_{38}ON_2$ .

The crude base was first purified by crystallisation from ethyl acetate, when it melted at  $190^\circ$ , and then converted into the hydrobromide. This salt was crystallised from water and washed with acetone. It was then reconverted into the base, and this was recrystallised from ethyl acetate, when it separated in silky needles which melted at  $197-198^\circ$  (corr.). It suffers no loss at  $100^\circ$ . It is insoluble in water, readily soluble in alcohol or chloroform, but sparingly so in cold ethyl acetate, acetone, or ether.

Found: C = 77.5, 77.6, 77.3; H = 10.2, 10.3, 10.7; N = 7.7;

Me(attached to N) = 11.1, 12.2.

$C_{24}H_{38}ON_2$  (370.4) requires C = 77.8; H = 10.3; N = 7.6;

Me(attached to N) = 12.2 per cent.

The specific rotatory power was determined in chloroform solution:

$\alpha_D - 0.75^\circ$ ;  $c = 5.248$ ;  $l = 2$  dcm.;  $[\alpha]_D - 7.1^\circ$ .

The *hydrobromide* crystallises from water in flat needles, which melt at  $265-268^\circ$  (corr.) after drying. It is readily soluble in hot, somewhat sparingly so in cold, water. The air-dried salt contains  $3H_2O$  (Found:  $H_2O = 9.0$ . Calc.:  $H_2O = 9.2$  per cent.).

Found, in salt dried at  $100^\circ$ , C = 54.4; H = 8.2; Br = 29.8.

$C_{24}H_{38}ON_2 \cdot 2HBr$  (532.3) requires C = 54.1; H = 7.6; Br = 30.0 per cent.

The specific rotatory power was determined in aqueous solution:

$\alpha_D + 1.02^\circ$ ;  $c = 4.630$ ;  $l = 2$  dcm.;  $[\alpha]_D + 11.0^\circ$  or  $+12.1^\circ$  for the anhydrous salt.

*Acetylholarrhenine*, prepared by the action of acetic anhydride and anhydrous sodium acetate on holarrhenine, crystallises from acetone in large, colourless, oblong plates which melt at  $180^\circ$  (corr.).

It is insoluble in water, sparingly soluble in cold alcohol, acetone, or ether, but readily so in chloroform.

Found: C=75·7; H=9·9; N=6·8.

Equivalent to HCl, using methyl-orange=202.

$C_{26}H_{40}O_9N_2$  (412·5) requires C=75·7; H=9·8; N=6·8 per cent.

THE WELLCOME CHEMICAL WORKS.

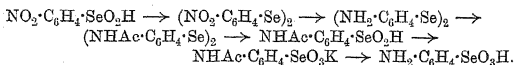
DARTFORD, KENT,

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## XIX.—*Meta-substituted Aromatic Selenium Compounds.*

By FRANK LEE PYMAN.

At the suggestion of Dr. Charles Walker, of Glasgow, attempts were made, in 1913, to form the selenium analogue of arsanilic acid, namely, *p*-aminophenylselenic acid,  $NH_2 \cdot C_6H_4 \cdot SeO_3H$ , in order to determine its physiological action. Whilst aniline sulphate and arsenate readily yield sulphanilic acid and arsanilic acid, respectively, at an elevated temperature, no similar compound could be obtained from aniline selenate. It was found, however, that phenylselenious acid gave on nitration a *nitrophenylselenious acid*, which is shown to be the meta-compound in the manner described below. On reducing this compound with sodium hydrogen sulphite, *di-m-nitrophenyl diselenide* resulted, and gave *di-m-aminophenyl diselenide* on further reduction with sodium sulphide. *Di-m-aminophenyl diselenide* gave on acetylation *di-m-acetylaminophenyl diselenide*, from which *m-acetylaminophenylselenious acid* was obtained by oxidation with nitric acid. From this, the salts of *m-acetylaminophenylselenic acid* were obtained on oxidation with potassium permanganate, whilst on attempting to liberate the free acid, hydrolysis took place with the formation of *m-aminophenylselenic acid*:



When these results were first communicated to the Society (P., 1914, 30, 302), the orientation of the nitro-group in nitrophenylselenious acid had not been determined, and in the discussion on the paper, Dr. Tuck suggested that the constitution of this acid might be settled by preparing the three isomerides by the action



of the nitrobenzenediazonium chlorides on potassium selenocyanate and suitable after-treatment. This method had already been applied by Bauer (*Ber.*, 1913, **46**, 92) to the preparation of *o*-nitrophenyl selenocyanate, and by Morgan and Elliot (*P.*, 1914, **30**, 248) to the preparation of *p*-chlorophenyl selenocyanate and their derivatives.

At the author's request, Mr. H. King has now kindly prepared *m*-nitrophenyl selenocyanate, from which he has obtained, on reduction with tin and hydrochloric acid, di-*m*-aminophenyl diselenide, identical with the product resulting from the reduction of nitrophenylselenious acid, thereby proving the constitution of the compounds described above.

#### EXPERIMENTAL.

##### *Phenylselenious Acid*, $\text{PhSeO}_2\text{H}$ .

The preparation of this acid and its nitrate have been described by Stoecker and Krafft (*Ber.*, 1906, **39**, 2197). Diphenyl diselenide (1 part by weight) was dissolved in concentrated nitric acid (40 parts by weight) and heated. On cooling, the well-crystallised nitrate of phenylselenious acid separated. In order to liberate the free acid, the nitrate was dissolved in ammonia and mixed with silver nitrate, when silver phenylselenite was precipitated, and gave the free acid when decomposed with the equivalent quantity of hydrochloric acid.

Doughty (*Amer. Chem. J.*, 1909, **41**, 326) subsequently obtained this acid by the action of hydrochloric acid on phenylselenic acid resulting from the interaction of selenic acid and benzene. He was unable to confirm the previous author's statement that the acid crystallised with  $2\text{H}_2\text{O}$ , finding it to be anhydrous.

For the purpose of the present investigation, considerable quantities of this acid were required, and a modification of Stoecker and Krafft's process was adopted. Instead of employing pure diphenyl diselenide, the mixture of this substance with selenophenol, obtained by the action of selenium on magnesium phenyl bromide (Taboury, *Bull. Soc. chim.*, 1903, [iii], **29**, 761), was used. On treating this with 4 c.c.—instead of 30 c.c.—of nitric acid for each gram, phenylselenious acid nitrate was readily prepared in quantity. When mixed with sufficient ammonia to neutralise the nitric acid, it gave free phenylselenious acid, which was found to be practically anhydrous, in agreement with Doughty's observation.

To a solution of magnesium phenyl bromide in dry ether, prepared from 24 grams of magnesium and 157 grams of bromo-

benzene, 79 grams of selenium were added gradually, and the mixture was boiled for half an hour. The product was decomposed with ice and dilute hydrochloric acid, well shaken, and the ethereal layer removed, the aqueous layer being extracted with ether twice again. The ethereal extracts were combined, dried with calcium chloride, and the solvent was removed on the water-bath. The resulting oil (about 130 grams) was then allowed to flow drop by drop into concentrated nitric acid (D 1.4), of which 4 c.c. were employed for each gram of the oil. The nitric acid solution was then digested for an hour on the water-bath and kept, when crude phenylselenious acid nitrate separated in hard crystals. This was collected on asbestos, dissolved in water, and the solution filtered from insoluble matter. The solution was then extracted with ether to remove further impurities, and evaporated to a syrup. On cooling, this set to a chalky mass of the nearly pure nitrate, which, after thorough drying in the air, amounted to about 110 grams. The yield is thus 44 per cent. of the theoretical.

For the preparation of the free acid, 10 grams of the nitrate were dissolved in 20 c.c. of water, and 6 c.c. of 10 per cent. aqueous ammonium hydroxide added. On stirring, phenylselenious acid separated in sandy, yellow grains, which were purified by crystallisation from water. 6.5 Grams of the pure acid were isolated without carrying out the separation to an end, whilst 7.6 grams are required theoretically. Phenylselenious acid, prepared in this way, melted at 124—125° (corr.) after drying at 100°. The air-dried acid was practically anhydrous. (Found, loss at 100°=0.4; C=37.6; H=3.3.  $C_6H_5 \cdot SeO_2H$  requires C=38.0; H=3.2 per cent.)

*Sodium phenylselenite* crystallises from water in colourless plates containing  $2H_2O$ . It is readily soluble in water.

Found, loss at 100°, 14.6.

$C_6H_5 \cdot SeO_2Na \cdot 2H_2O$  (247.2) requires  $H_2O=14.6$  per cent.

Found, in anhydrous salt, Se=37.9, 37.5.\*

$C_6H_5 \cdot SeO_2Na$  requires Se=37.5 per cent.

#### *Salts of Phenylselenic Acid.*

Stoecker and Krafft (*loc. cit.*) prepared phenylselenic acid by the oxidation of diphenyl diselenide with moist chlorine, Doughty by the method given above (*loc. cit.*). The potassium salt can be obtained conveniently by oxidising phenylselenious acid with

\* For the estimation of selenium in the compounds described in this paper Frerichs's method (*Arch. Pharm.*, 1902, 240, 656) was employed.

potassium permanganate, removing manganese dioxide, and evaporating to low bulk, when it crystallises from the solution.

*Potassium phenylselenate* forms colourless, prismatic needles which, after being dried in the air, sinter from about  $50^{\circ}$  and melt from  $65^{\circ}$  to  $90^{\circ}$  in the water of crystallisation. It is readily soluble in cold, and very readily so in hot, water.

Found, loss in a vacuum over  $\text{H}_2\text{SO}_4$  and then at  $100^{\circ}$ , 12.7.

$\text{C}_6\text{H}_5\cdot\text{SeO}_3\text{K}\cdot 2\text{H}_2\text{O}$  (279.4) requires  $\text{H}_2\text{O}=12.9$  per cent.

Found, in anhydrous salt,  $\text{Se}=32.2$ .

$\text{C}_6\text{H}_5\cdot\text{SeO}_3\text{K}$  requires  $\text{Se}=32.6$  per cent.

*Sodium phenylselenate* was prepared from the barium salt, which has been described by Doughty (*loc. cit.*), by double decomposition with sodium sulphate. It crystallises from water in long, clear, oblong plates which contain  $3\text{H}_2\text{O}$ , and is readily soluble in cold, very readily so in hot water.

Found, in air-dried salt: loss at  $120^{\circ}=24.2$ ;  $\text{Se}=26.5$ .

$\text{C}_6\text{H}_5\cdot\text{SeO}_3\text{Na}\cdot 4\text{H}_2\text{O}$  (299.2) requires  $\text{H}_2\text{O}=24.1$ ;  $\text{Se}=26.5$  per cent.

#### *m-Nitrophenylselenious Acid*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SeO}_2\text{H}$ .

Phenylselenious acid did not yield a nitro-derivative when treated with a mixture of sulphuric and nitric acids at  $100^{\circ}$ . When subjected to the action of a large excess of fuming nitric acid at  $150^{\circ}$  for one hour, it gave a 20 per cent. yield of *m*-nitrophenylselenious acid. The best method for the preparation of this acid, however, was found in the action of nascent nitric acid generated from potassium nitrate.

Thirty grams of phenylselenious acid nitrate were dissolved in 30 c.c. of sulphuric acid, and the solution was cooled with running water. Twelve grams of finely powdered potassium nitrate were then stirred into the solution, which was similarly cooled. The mixture was heated for two hours in the steam-bath, and poured into 600 c.c. of water. After keeping for several hours, the separated crystals were collected. They amounted to 17.4 to 18.7 grams of an almost pure product melting at  $155^{\circ}$  or slightly lower.

*m-Nitrophenylselenious acid* crystallises from water in yellow, prismatic needles, which melt at  $156\text{--}157^{\circ}$  (corr.) after drying at  $100^{\circ}$ . It is fairly readily soluble in boiling water, sparingly so in cold.

Found, loss at  $100^{\circ}=0.4$ ; in dried substance,  $\text{C}=30.8$ ;  $\text{H}=2.2$ .

$\text{C}_6\text{H}_5\text{O}_4\text{NSe}$  (234.2) requires  $\text{C}=30.8$ ;  $\text{H}=2.2$  per cent.

*m*-Nitrophenylselenic Acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SeO}_3\text{H}$ .

Thirty-five grams of *m*-nitrophenylselenious acid were dissolved in 600 c.c. of boiling water to which 20 c.c. of 10 per cent. aqueous potassium hydroxide had been added, and mixed with a solution of 16 grams of potassium permanganate in 200 c.c. of hot water. Further small quantities of permanganate were then added until the red colour no longer quickly vanished. The manganese dioxide was removed by filtration, and the solution evaporated to low bulk and cooled, when potassium *m*-nitrophenylselenate crystallised out. After purification by recrystallisation from water, 34 grams were obtained.

Potassium *m*-nitrophenylselenate forms hard, yellow rosettes of flat needles. It is anhydrous, and is readily soluble in hot, but somewhat sparingly so in cold, water. It explodes violently at about  $330^\circ$  (corr.).

Found: Se = 27.1.

$\text{C}_6\text{H}_4\text{O}_5\text{NKSe}$  (288.3) requires Se = 27.5 per cent.

Barium *m*-nitrophenylselenate was prepared from the potassium salt by double decomposition with the calculated quantity of barium chloride. It forms colourless leaflets which are fairly readily soluble in hot, but sparingly so in cold, water. It contains  $2\text{H}_2\text{O}$ , which are lost at  $120^\circ$ , but not at  $110^\circ$ .

Found, in air-dried salt, loss at  $120^\circ = 5.6$ . Ba = 20.2.

$\text{C}_{12}\text{H}_8\text{O}_{10}\text{N}_2\text{BaSe}_2 \cdot 2\text{H}_2\text{O}$  (671.9) requires  $\text{H}_2\text{O} = 5.4$ ; Ba = 20.5 per cent.

*m*-Nitrophenylselenic acid was prepared from the barium salt by the addition of the calculated quantity of sulphuric acid, removal of barium sulphate, and evaporation to a syrup, when it crystallised, on keeping, in colourless plates containing  $2\text{H}_2\text{O}$ . The air-dried acid melts below  $100^\circ$ , but after drying first in a vacuum over sulphuric acid, then at  $100^\circ$ , it is rendered anhydrous and then melts at  $146^\circ$  (corr.).

Found, loss at  $100^\circ = 12.8$ .

$\text{C}_6\text{H}_5\text{O}_5\text{NSe} \cdot 2\text{H}_2\text{O}$  (286.3) requires  $\text{H}_2\text{O} = 12.7$  per cent.

0.2379, dried at  $100^\circ$ , required 18.95 c.c. of *N*/20-NaOH for neutralisation, whence equivalent = 251.

$\text{C}_6\text{H}_5\text{O}_5\text{NSe}$  requires M.W. = 250.3.

*Di*-*m*-nitrophenyl Diselenide,  $(\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Se})_2$ .

Twenty-four grams of *m*-nitrophenylselenious acid were dissolved in 250 c.c. of boiling water, and a saturated solution of sodium

hydrogen sulphite was added so long as a turbidity was produced. After cooling and stirring, the oil which had separated became crystalline, and was collected and washed with water. The theoretical yield—20.5 grams—was obtained, and the product melted at 79°. After crystallisation from ether, this compound formed yellow spears which melted at 83° (corr.).

Found: C=35.6; H=2.2.

$C_{12}H_5O_4N_2Se_2$  (402.5) requires C=35.8; H=2.0 per cent.

It is insoluble in water, moderately readily soluble in cold alcohol or ether, fairly readily so in hot alcohol, and easily so in hot ether.

*Di-m-aminophenyl Diselenide,  $(NH_2 \cdot C_6H_4 \cdot Se)_2$ .*

Fifty grams of di-m-nitrophenyl diselenide were added to a solution of 300 grams of commercial hydrated sodium sulphide in 500 c.c. of 10 per cent. aqueous sodium hydroxide previously heated to about 60°, and the mixture was boiled for one hour under a reflux condenser. One litre of boiling water was then added, and an excess of concentrated hydrochloric acid. After digestion for two hours on the steam-bath, the separated sulphur was removed by filtration. The filtrate was cooled, basified with sodium carbonate, and extracted with ether. The ethereal solution was dried with anhydrous potassium carbonate and distilled. The residue was mixed with an excess of 10 per cent. hydrochloric acid, when 39.7 grams of di-m-aminophenyl diselenide dihydrochloride separated in sandy crystals.

*Di-m-aminophenyl diselenide dihydrochloride* crystallises from dilute hydrochloric acid in yellow grains formed of small needles. It melts and decomposes at 291—292° (corr.). It is readily soluble in hot, but sparingly so in cold, dilute hydrochloric acid.

Found, loss at 100°=1.1; in dried salt, C=35.3; H=3.5;

Se=37.5; Cl=16.8.

$C_{12}H_{12}N_2Se_2 \cdot 2HCl$  (415.4) requires C=34.7; H=3.4; Se=38.1; Cl=17.1 per cent.

*Di-m-acetylaminophenyl Diselenide,  $(CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot Se)_2$ .*

25.2 Grams of di-m-aminophenyl diselenide dihydrochloride were converted into the base, and this was treated with 25 c.c. of acetic anhydride. The clear liquid quickly began to crystallise, and soon set to a yellow, chalky mass, which was washed well with ether and dried in the air. 19.6 Grams of di-m-acetylaminophenyl diselenide

melting at  $180^{\circ}$  were thus obtained, the yield amounting to 76 per cent. of the theoretical.

For the preparation of this substance, the previous isolation of di-*m*-aminophenyl diselenide as the dihydrochloride is unnecessary; thus 91 grams of di-*m*-nitrophenyl diselenide were reduced by the method given previously, and the ethereal residue of crude di-*m*-aminophenyl diselenide was mixed with 50 c.c. of acetic anhydride and treated as above. The resulting di-*m*-acetylaminophenyl diselenide melted at  $179^{\circ}$  and amounted to 76 grams, that is, 79 per cent. of the theoretical.

*Di-m-acetylaminophenyl diselenide* crystallises from glacial acetic acid in rosettes of short, yellow needles which melt at  $185\text{--}186^{\circ}$  (corr.). It is anhydrous, and is insoluble in hot or cold water, almost insoluble in hot or cold ether, readily soluble in hot alcohol or glacial acetic acid, but sparingly so in these solvents when cold.

Found: C=45.0; H=4.0.

$\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2\text{Se}_2$  (426.6) requires C=45.0; H=3.8 per cent.

*Formation of Di-m-aminophenyl Diselenide by the Reduction of m-Nitrophenyl Selenocyanate.*

*m*-Nitroaniline (6.9 grams) was diazotised in dilute hydrochloric acid solution at  $0^{\circ}$ , and, after filtering from 1 gram of diazoamino-compound, the acidity of the solution to Congo paper was removed by the addition of 10 grams of sodium acetate crystals. Potassium selenocyanate (7.2 grams) dissolved in a little water was added slowly with stirring. There was a brisk evolution of nitrogen accompanied by the separation of a red oil. On washing with water, the latter gradually solidified, and was dissolved in ether to free it from selenium powder (0.6 gram). The ethereal solution was concentrated, again filtered from a small quantity of a viscous red oil, and finally evaporated to a syrup, which crystallised on stirring. The product consisted of transparent crystals embedded in a small quantity of a deep red gum. The yield of crude *m*-nitrophenyl selenocyanate was 7.2 grams, or 73 per cent. of theory.

The crude product (3.4 grams) was dissolved in hot alcohol (50 c.c.) and reduced by boiling for one hour with tin (3.5 grams) and hydrochloric acid (45 c.c.; 32 per cent.). On concentration under diminished pressure, the hot solution deposited an orange-yellow, granular, crystalline stannichloride (5.8 grams).

One gram of the stannichloride was dissolved in water, and the tin removed as sulphide. The solution, on concentration, gave two

successive separations of crystalline di-*m*-aminophenyl diselenide dihydrochloride, 0.2 gram and 0.25 gram, each melting at 278–280° (uncorr.). (Found: Cl=17.0. Calc.: Cl=17.1 per cent.) Di-*m*-aminophenyl diselenide dihydrochloride, obtained by the reduction of di-*m*-nitrophenyl diselenide, melted at the same temperature as did a mixture of the two. Moreover, both form a sparingly soluble, primrose-yellow stannochloride crystallising in microscopic needles, and a stannichloride which tends to separate as an oil from cold solutions, but in granular crystals from hot solutions.

Acetylation of the di-*m*-aminophenyl diselenide, prepared from *m*-nitrophenyl selenocyanate, gave di-*m*-acetylaminophenyl diselenide in short needles which melted at 183–185° (uncorr.), the acetyl derivative of the reduction product of di-*m*-nitrophenyl diselenide melting at the same temperature, whilst a mixture of the two showed no depression of the melting point.

*m*-Acetylaminophenylselenious Acid,  $\text{CH}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SeO}_2\text{H}$ .

Ten grams of di-*m*-acetylaminophenyl diselenide were added with stirring in quantities of about 1 gram to 40 c.c. of nitric acid (D 1.4) kept at –6° to –3°. At first, the diselenide dissolved, giving a clear solution, but the separation of white crystals soon commenced, and increased on the further addition of this substance. The crystals were collected on asbestos, washed with concentrated nitric acid, and drained on porous porcelain. This substance melted at 146°, and was the nitrate of *m*-acetylaminophenylselenious acid. After grinding it with water, filtering, and washing with water, crude *m*-acetylaminophenylselenious acid, melting at 201°, remained undissolved. The product at this stage still contained nitric acid, and a portion, on boiling with water with the view of recrystallising it, readily oxidised. The whole was therefore dissolved in an excess of hot dilute ammonia (200 c.c.), treated with animal charcoal, filtered, and acidified with glacial acetic acid. On keeping, *m*-acetylaminophenylselenious acid crystallised in fine, colourless needles, which were collected, washed well with water, and dried in the air. The yield amounted to 8.5 grams of the pure acid.

*m*-Acetylaminophenylselenious acid crystallises from boiling water in short, slender, colourless needles, which begin to turn brown at about 200° and melt and decompose at 209° (corr.). It is sparingly soluble in hot, very sparingly so in cold, water.

Found: C=39.5, 39.5; H=3.7, 3.8.

$\text{C}_8\text{H}_9\text{O}_3\text{NSe}$  (246.3) requires C=39.0; H=3.7 per cent.

*Sodium m-acetylaminophenylselenite* crystallises from water in microscopic needles. After drying in the air, this salt contains  $7\text{H}_2\text{O}$ , of which 4 are lost at  $100^\circ$  and the remainder at  $120^\circ$ . It is fairly readily soluble in cold and easily so in hot water.

Found: loss at  $100^\circ=18.2$ ; loss at  $120^\circ=32.2$ .

$\text{C}_8\text{H}_8\text{O}_3\text{NNaSe}\cdot 7\text{H}_2\text{O}$  (394.4) requires  $4\text{H}_2\text{O}=18.3$ ;  $7\text{H}_2\text{O}=32.0$  per cent.

*Salts of m-Acetylaminophenylselenic Acid,*  
 $\text{CH}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SeO}_3\text{H}.$

Fifty-five grams of *m*-acetylaminophenylselenious acid were dissolved in 70 c.c. of 10 per cent. ammonia and a litre of hot water, and mixed with a hot aqueous solution of 26 grams of potassium permanganate. After digestion for a few minutes on the water-bath, the slight excess of permanganate was reduced by means of alcohol. The solution was boiled, filtered from manganese hydroxide, and 28.5 grams of barium nitrate were dissolved in it. On evaporating to a small volume and keeping, barium *m*-acetylaminophenylselenate crystallised out. After recrystallisation from water, 48 grams of the pure salt were obtained. A considerable further quantity was subsequently isolated from the mother liquors.

*Barium m-acetylaminophenylselenate* crystallises from water in hard, colourless, flat needles containing  $4\text{H}_2\text{O}$ . It is fairly readily soluble in cold, very readily so in hot, water.

Found: loss at  $120^\circ=10.1$ .

$\text{C}_{16}\text{H}_{16}\text{O}_8\text{N}_2\text{BaSe}_2\cdot 4\text{H}_2\text{O}$  (732.0) requires  $\text{H}_2\text{O}=9.8$  per cent.

Found, in dried salt,  $\text{Ba}=20.8$ .

$\text{C}_{16}\text{H}_{16}\text{O}_8\text{N}_2\text{BaSe}_2$  requires  $\text{Ba}=20.8$  per cent.

*Sodium m-acetylaminophenylselenate* was prepared from the barium salt by double decomposition with sodium sulphate. It crystallises from water in colourless, woolly needles, and from alcohol in prismatic needles, in both cases without solvent of crystallisation. It is very readily soluble in water, sparingly so in cold alcohol, but fairly readily so in hot alcohol.

Found:  $\text{Se}=27.9$ .

$\text{C}_8\text{H}_8\text{O}_4\text{NNaSe}$  (284.2) requires  $\text{Se}=27.9$  per cent.

*m-Aminophenylselenic Acid,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SeO}_3\text{H}.$*

Forty-five grams of barium *m*-acetylaminophenylselenate were dissolved in 500 c.c. of boiling water, and sufficient sulphuric acid



was added exactly to remove the barium. The solution was then boiled, filtered from barium sulphate, and evaporated to a small volume under diminished pressure, when 13 grams of *m*-aminophenylselenic acid crystallised from the solution.

*m*-Aminophenylselenic acid crystallises from water in colourless needles which contain  $2\text{H}_2\text{O}$ , and, after drying at  $100^\circ$ , melts and decomposes at  $229^\circ$  (corr.). It is readily soluble in hot, sparingly so in cold, water.

Found, in air-dried substance, loss at  $100^\circ = 11.4$ .

$\text{C}_6\text{H}_7\text{O}_3\text{NSe}, 1\frac{1}{2}\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 10.9$  per cent.

Found, in dried substance,  $\text{C} = 32.7$ ;  $\text{H} = 3.3$ .

$\text{C}_6\text{H}_7\text{O}_3\text{NSe}$  (220.3) requires  $\text{C} = 32.7$ ;  $\text{H} = 3.2$  per cent.

Sodium *m*-aminophenylselenate crystallises from water in plates, which are readily soluble in cold water.

Found, in air-dried salt, loss at  $120^\circ = 19.9$ .

$\text{C}_6\text{H}_6\text{O}_3\text{NNaSe}, 3\frac{1}{2}\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 20.6$  per cent.

Found, in dried salt,  $\text{Se} = 33.0$ .

$\text{C}_6\text{H}_6\text{O}_3\text{NNaSe}$  (242.2) requires  $\text{Se} = 32.7$  per cent.

THE WELLCOME CHEMICAL WORKS,  
DARTFORD, KENT.

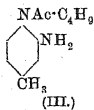
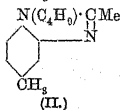
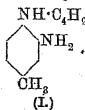
[Received, February 4th, 1919.]

## XX.—The *n*-Butylarylamines. Part III. Constitution of the Nitro-derivatives of *n*-Butyl-*p*-toluidine.

By JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM.

IN Part II. of this series (T., 1918, 113, 985), the preparation of 2- and 3-nitro-*n*-butyl-*p*-toluidines was described, and in the present paper an account is given of the products of reduction of these nitro-compounds, the study of which has shown that the constitutions previously assigned to them are correct.

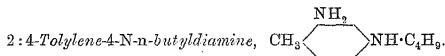
The 3-nitro-derivative, on reduction, furnishes 3:4-tolylene-4-*N*-*n*-butyldiamine (I), which is a readily oxidisable oil, and the corresponding 3-nitroacetyl derivative gives 2:5-dimethyl-1-*n*-butylbenzimidazole (II), which is also obtained by the action of heat on 4-acetyl-3:4-tolylene-4-*N*-*n*-butyldiamine (III).



The constitution of 3:5-dinitro-*n*-butyl-*p*-toluidine is proved by the fact that on hydrolysis with sodium hydroxide it yields *n*-butylamine and 3:5-dinitro-*p*-cresol.

By the action of acids or direct sunlight on 3:5-dinitro-*p*-tolyl-*n*-butyl-nitro- or -nitroso-amine, the dinitro-amine is regenerated, and the nitroamine is similarly decomposed on boiling it with ethyl or *n*-butyl alcohols. When the nitroamine is hydrolysed by sulphuric acid or sodium hydroxide, nitrous acid is formed.

#### EXPERIMENTAL.



2-Nitro-*n*-butyl-*p*-toluidine (3 grams) was mixed with 10 c.c. of concentrated hydrochloric acid and 40 c.c. of water, and zinc dust (4 grams) gradually added. Excess of zinc was removed from the colourless solution, and the amine was isolated by the addition of sodium hydroxide solution, followed by extraction with ether. It formed a pale brown powder, which was purified by solution in dry ether and precipitation with light petroleum. A white, flocculent mass was obtained which, on drying, could easily be powdered. By spontaneous evaporation of the ethereal solution, it was obtained in colourless needles melting at 53°:

0.0956 gave 12.9 c.c.  $\text{N}_2$  at 19.2° and 750 mm.  $\text{N} = 15.56\%$

$\text{C}_{11}\text{H}_{18}\text{N}_2$  requires  $\text{N} = 15.72$  per cent.

2:4-Tolylene-4-N-*n*-butyldiamine is soluble in most of the common organic solvents, sparingly so in water, and very sparingly so in light petroleum. With ferric chloride solution, it gives a very faint brown coloration, which, however, is not very characteristic. It gives no characteristic colour with nitrous acid or potassium ferrocyanide. The hydrochloride is very readily soluble in water.

*4-Acetyl Derivative.*—Tin foil was added to 2-nitroaceto-*n*-butyl-*p*-toluidide (1 mol.) suspended in concentrated hydrochloric acid (6 mols.) until reduction was complete. The solution was filtered, diluted with water, and the tin removed by means of hydrogen sulphide. The filtrate was rendered alkaline and the amine isolated, as a brown oil, by extraction with ether. It solidified to a mass of brown crystals, which on crystallisation from a mixture

\* In the nitrogen estimations recorded in this paper, the gas was collected over 40 per cent. potassium hydroxide solution. A correction has been introduced for the vapour tension of the potassium hydroxide solution.

of ether and light petroleum was obtained in white crystals melting at 98—99°:

0.0723 gave 8.1 c.c.  $N_2$  at 20° and 749 mm.  $N=12.87$ .

$C_{13}H_{20}ON_2$  requires  $N=12.72$  per cent.

The compound dissolves in ether and many of the other organic solvents, but is insoluble in light petroleum. The diazo-compound gives with  $\beta$ -naphthol a brownish-red *azo-dye*, which dissolves in sulphuric acid with the development of a deep purple-red coloration, changing to pale brown on dilution. The *picrate* of the base crystallises from alcohol in groups of yellow needles melting at 185°.

#### 3:4-Tolylene-4-N-n-butyl-diamine.

The reduction of 3-nitro-*n*-butyl-*p*-toluidine in the way described for the 2-nitro-compound, yields the corresponding diamine as an oil, which is white when first precipitated, but rapidly acquires a deep blue colour and ultimately becomes almost black:

0.1211 gave 16.2 c.c.  $N_2$  at 22° and 764 mm.  $N=15.57$ .

$C_{11}H_{18}N_2$  requires  $N=15.72$  per cent.

The compound is readily miscible with most of the ordinary organic solvents. The *hydrochloride* was obtained by passing a stream of dry hydrogen chloride into a solution of the base in dry xylene. The bulk of the xylene was decanted, and the rest removed by washing with light petroleum. After being dried at 100°, the salt formed a white powder. It is extremely deliquescent and very readily soluble in water:

0.0552 gave 0.0625 AgCl.  $Cl=28.0$ .

$C_{11}H_{18}N_2 \cdot 2HCl$  requires  $Cl=28.2$  per cent.

The aqueous solution is very readily oxidised. One drop of ferric chloride solution produces an intense blood-red or deep brown colour. A dilute solution of chromic acid or a very dilute neutral solution of potassium dichromate produces a brownish-black or black solution, depending on the concentration of the oxidising agent. An aqueous solution of bleaching powder yields a deep blue solution. Nitrous acid in dilute solution gives a dirty purple coloration, whilst concentrated nitric acid also gives a purple coloration.

The 3:4-*diacetyl* derivative was prepared by warming the base with acetic anhydride. A dark-coloured oil was obtained, which slowly solidified to a mass of dark brown crystals. By repeated crystallisation from a mixture of light petroleum and acetone, or

from hot dilute aqueous alcohol, it was obtained in white crystals melting at  $130^{\circ}$ :

0.0754 gave 7.1 c.c.  $N_2$  at  $25^{\circ}$  and 748 mm.  $N=10.62$ .

$C_{15}H_{22}O_2N_2$  requires  $N=10.69$  per cent.

The compound is moderately soluble in hot, but sparingly so in cold water.

#### 4-Acetyl-3:4-tolylene-4-N-n-butylldiamine (III).

3-Nitroaceto-*n*-butyl-*p*-toluidide (4 grams) was dissolved in 50 c.c. of aqueous alcohol (70 per cent.) containing iron filings (10 grams), and to the mixture, warmed to  $30^{\circ}$ , glacial acetic acid was slowly added, the temperature being kept at  $30^{\circ}$ . After an hour, the mixture was heated on the water-bath, the unchanged iron removed by filtration, washed with warm dilute acetic acid, and the filtrate rendered alkaline and heated at  $80^{\circ}$  for several hours. The base was extracted with ether and purified by recrystallisation from a mixture of equal parts of dry ether and light petroleum, when it was obtained in short, colourless needles melting at  $102^{\circ}$ :

0.0702 gave 8.0 c.c.  $N_2$  at  $21^{\circ}$  and 738 mm.  $N=12.85$ .

$C_{13}H_{20}ON_2$  requires  $N=12.72$  per cent.

The compound is readily soluble in alcohol, ether, benzene, or carbon tetrachloride, but very sparingly so in light petroleum. The diazo-compound gives a red *azo-dye* with  $\beta$ -naphthol. On heating the base in a flask fitted with a short air condenser at  $200^{\circ}$  in an oil-bath, globules of water were observed in the condenser. After heating for four to five hours, the dark, viscous residue was distilled over a free flame, when a pale yellow oil was obtained which did not solidify at  $0^{\circ}$ , and was not a primary amine. From its method of formation, it is probably 2:5-dimethyl-1-n-butylbenzimidazole (II). The same compound was produced by the vigorous reduction of 3-nitroaceto-*n*-butyl-*p*-toluidide in acid solution.

The nitro-compound (5 grams) was dissolved in a mixture of glacial acetic acid (25 grams), concentrated hydrochloric acid (10 grams), and water (15 c.c.). Zinc dust (20 grams) was added, and the solution became very warm. After the reaction had moderated and more zinc dust had been added, the solution was heated on the sand-bath for one or two hours. After removal of the excess of zinc, the solution was rendered alkaline with potassium hydroxide solution, and the precipitated oil extracted with ether.

On distillation, it was obtained as a very viscous, pale yellow oil boiling at 335—338°:

0.0746 gave 0.2115 CO<sub>2</sub> and 0.0606 H<sub>2</sub>O. C=77.34; H=9.09.

0.0794 „ 9.9 c.c. N<sub>2</sub> at 23.1° and 736 mm. N=13.92.

C<sub>13</sub>H<sub>18</sub>N<sub>2</sub> requires C=77.18; H=8.97; N=13.85 per cent.

2:5-Dimethyl-1-*n*-butylbenzimidazole is miscible with ether or alcohol. When exposed in an open dish to a moist atmosphere, it readily absorbs water and oxygen, gradually becoming darker. By the action of an aqueous-alcoholic solution of picric acid on the alcoholic solution of the anhydro-base, the *picrate* was precipitated; this crystallised from acetone in short, yellow needles or prisms melting at 209°:

0.0756 gave 10.7 c.c. N<sub>2</sub> at 21° and 749 mm. N=16.20.

C<sub>13</sub>H<sub>18</sub>N<sub>2</sub>.C<sub>6</sub>H<sub>3</sub>O<sub>7</sub>N<sub>3</sub> requires N=16.24 per cent.

It is practically insoluble in water, ether, or alcohol.

*Action of Alkalis on 3:5-Dinitro-n-butyl-p-toluidine.*

The dinitro-compound (1 gram) was heated under reflux with a solution of 5 grams of potassium hydroxide in 40 c.c. of water for six to eight hours. The colour of the solution changed rapidly through brownish-red to very dark red or almost black. On distillation into dilute hydrochloric acid, *n*-butylamine hydrochloride was obtained. The alkaline residue in the flask, after being cooled and filtered, was acidified with dilute sulphuric acid, and from the ethereal extract a solid crystallising in yellow needles (m. p. 82°) was obtained, which proved to be 3:5-dinitro-*p*-cresol.

*Action of Acids on 3:5-Dinitro-p-tolyl-n-butyl-nitroamine and -nitrosoamine.*

3:5-Dinitro-*p*-tolyl-*n*-butylnitroamine (0.5 gram) was dissolved in 2 c.c. of concentrated sulphuric acid (97 per cent.), the solution being kept cool by immersion in ice-cold water. The nitroamine dissolved slowly with the production of a deep reddish-purple colour, which changed finally to yellow. After half an hour, the mixture was poured on ice, when a yellow solid was obtained, which proved to be the corresponding nitrosoamine. Nitrous acid was also found to be present. In another experiment, 50 c.c. of slightly warmed sulphuric acid (90 per cent.) were added to the nitroamine (0.5 gram). There was a faint odour of nitrous acid, and the colour changes were the same as those described above.

After remaining for twenty days, exposed for part of the time to sunlight, the colour had changed to deep red. On pouring into water and extracting with ether, 3:5-dinitro-*n*-butyl-*p*-toluidine was obtained as the chief product. Further, the nitroamine (0.5 gram) was heated under reflux with a mixture of concentrated hydrochloric acid (20 c.c.) and *n*-butyl alcohol (50 c.c.) for eight hours. The colour of the mixture gradually became darker until it was finally a deep red. After removal of the alcohol, a red substance melting indefinitely at 65—80° was obtained. The melting point was raised to 86—88° by treatment with amyl nitrite in the presence of hydrochloric acid, the colour also becoming considerably paler.

On warming the nitroamine with an aqueous solution of perchloric acid and allowing the mixture to remain for twelve hours, a slight darkening occurred. The action of glacial phosphoric acid in the cold produced practically no colour change after a week.

3:5-Dinitro-*p*-tolyl-*n*-butylnitrosoamine, by the action of hydrochloric acid containing some aniline hydrochloride, yields the corresponding amine in almost quantitative yield and in a pure condition (compare Pinnow, *Ber.*, 1897, 30, 838). The nitrosoamine (2.4 grams) was heated under reflux for eight hours with alcoholic hydrogen chloride (50 c.c.) containing aniline hydrochloride (1 gram). On evaporating the alcohol, 2.1 grams of 3:5-dinitro-*n*-butyl-*p*-toluidine, identified by the mixed melting-point method, were obtained. When the aniline hydrochloride was omitted, the reaction followed a similar course, but required a longer time for completion.

*Action of Alkalis on 3:5-Dinitro-p-tolyl-n-butyl-nitroamine and -nitrosoamine.*

Alcoholic potassium hydroxide reacts with alcoholic solutions of the nitroamine and nitrosoamine with the production of a dark purple colour, which gradually deepens in intensity. In aqueous solution, the reaction takes place much more slowly. 3:5-Dinitro-*p*-tolyl-*n*-butylnitroamine (1 mol.) was heated under reflux with a large excess of a 10 per cent. aqueous solution of sodium hydroxide (15 mols.). The nitroamine was slowly attacked, yielding a purple solution which gradually became almost black, when the reaction was considered to be complete. On distillation, *n*-butylamine was obtained. The alkaline residue in the flask, which contained sodium nitrite, was diluted, and, after filtering, rendered acid in the presence of carbamide to remove nitrous acid. On extraction

with ether, a pale brown oil was obtained, which solidified to a yellow, crystalline solid. After several crystallisations from aqueous alcohol, this melted at 82°, and was shown to be 3:5-dinitro-*p*-cresol.

When either the nitroamine or the nitrosoamine was heated with two or three times its weight of phenol at 180°, and the product treated with very dilute ice-cold sodium hydroxide solution, followed by extraction with ether, 3:5-dinitro-*n*-butyl-*p*-toluidine was obtained in good yield, and the same result was obtained by heating the nitroamine or nitrosoamine with a large excess of *n*-butyl alcohol or ethyl alcohol for several hours in diffused light.

Both the nitroamine and nitrosoamine were finely powdered and exposed in glass and quartz vessels to direct sunlight. After one hour, the nitrosoamine had deepened considerably in colour, and the melting point was depressed. The nitroamine, on the other hand, changed colour only slowly, but there was sufficient action in both cases after one month's exposure to detect the presence of 3:5-dinitro-*n*-butyl-*p*-toluidine. In some of the reactions where the decomposition was not complete, the melting point alone was not a sufficient guide to determine the composition of the product. The colour affords an indication of the production of the parent amine, and this was confirmed by the evidence obtained by the action of amyl nitrite and of nitric acid. In the decomposition of the nitrosoamine or of the nitroamine, the production of the parent amine was assumed to have occurred when the action of amyl nitrite or nitrous acid in the presence of hydrochloric acid or acetic acid effected a considerable loss of colour, and when the melting point was altered. The action of fuming nitric acid in giving a product identical with the original nitroamine showed that the butyl group had not been removed and that only the nitroso-group linked to the aminic nitrogen atom had been affected.

[Received, January 16th, 1919.]

XXI.—*Studies in Catalysis. Part X. The Applicability of the Radiation Hypothesis to Heterogeneous Reactions.*

By WILLIAM CUDMORE McCULLAGH LEWIS.

In the previous papers of this series, the radiation hypothesis has been applied exclusively to reactions in homogeneous systems. A mode of applying the hypothesis to reactions in heterogeneous systems, including heterogeneous catalysis, having suggested itself to the author more than two years ago, it may not be out of place to indicate it briefly here.

In attempting to elucidate the mechanism of any chemical or physical process, two complementary methods of treatment may be employed. In the first, the process is considered from the point of view of the material or molecular changes involved; in the second, from the point of view of the concomitant or precedent energy exchanges. The radiation hypothesis belongs to the second method of treatment. The two methods are not distinct in the sense that the results obtained in one often furnish a clue to the solution of a difficulty met with in the other. It is necessary, however, to possess, in the first place, some information regarding the most probable material mechanism of the process considered before introducing considerations based on the energy exchanges involved. In the case of heterogeneous reactions and catalysis, Langmuir's theory of the spatial distribution of molecules and atoms at the interface between two phases will be adopted as a basis for the material changes occurring, the energy changes being then dealt with from the point of view of the radiation hypothesis.

Langmuir's theory (compare *J. Amer. Chem. Soc.*, 1916, **38**, 2221) is essentially an extension of the work of the Braggs on crystal structure.

The surface of a solid is regarded as a checker-board on which atoms or molecules of gases may be condensed by being united to certain atoms in the surface itself. This adsorption effect is ascribed directly to valency, in some cases the surface being almost entirely covered or saturated, in others only a small fraction of the surface being thus occupied. According to Langmuir, this surface layer does not consist of several layers of molecules or atoms in which the density varies continuously. Instead, the change from solid to homogeneous gas is abrupt. This is based on the idea that it is only a layer one molecule or atom in thickness



which would be held sufficiently firmly to the surface, especially at the moderately high temperatures at which heterogeneous reactions proceed in general with measurable velocity. Langmuir's experimental results support this view in many cases. When a gas molecule strikes a surface, it is in general condensed. The rate at which it evaporates depends on the chemical or specific nature of the molecule and of the layer of atoms in the surface of the solid. Thus nitrogen, in which the atoms are already very completely saturated, possesses only a feeble external field of force, and in the *molecular* form, therefore, will be only slightly adsorbed.

Langmuir has found that hydrogen in the *atomic* form, produced by heating a wire in dry hydrogen at very low pressures, has a remarkable tendency to be adsorbed, this being regarded as due to the unsaturated affinity of the hydrogen atom. Langmuir has calculated that in this case the adsorbed layer of gas is just one atom in thickness. Oxygen is likewise easily adsorbed by metallic (tungsten) filaments. This adsorbed layer is exceedingly stable, and is evidently distinct from the formation of the compound  $\text{WO}_3$ , which volatilises easily in comparison. On Langmuir's view, the oxygen is retained on the surface in the atomic form. A molecule or atom which is strongly adsorbed is capable of displacing one which is feebly adsorbed. Hence addition of a strongly adsorbed gas—which in certain cases may be the resultant of the reaction—may cover the surface of a solid more or less completely, the surface being thereby "poisoned" with respect to a reaction in which the reactants are only feebly adsorbed. Langmuir has given several instances of such effects. The essential point for our present purpose is the dissociation, partial or complete, which many substances undergo into the atomic state on being condensed on surfaces, the cause of such dissociation being the localised valencies or lines of force which hold the atoms of the condensed substance to certain atoms of the surface of the solid.\*

So much for the nature of the material changes involved. We have now to see how far the radiation hypothesis may assist in extending this view of the mechanism of the process.

In general, the velocity constants of heterogeneous reactions are characterised by possessing smaller temperature coefficients than those which are possessed by reactions in homogeneous systems. This means, on the basis of the considerations developed in earlier papers, that the critical increment in the heterogeneous process is

\* The catalytic effect of traces of moisture in the activation of molecules and atoms, and therefore possibly of surfaces, is not considered in the present paper. The facts hitherto recorded point to the conclusion that water is effective where ions are required to enable the reaction to proceed.

less than it would be for the same process occurring in the homogeneous system. This, in fact, appears to be the basis of the accelerating or catalytic effect of a given surface as viewed from the energy required to effect the chemical change.

It has already been shown that the reactivity of a substance depends on the magnitude of its critical increment, that is, the amount of energy which must be added per molecule or per gram-molecule, in excess of the average energy content, in order to bring the molecule into the active state.

The higher the critical increment, the smaller is the reactivity or rate of reaction of the substance. This increment is taken account of by the exponential term which appears in the velocity expression developed in previous papers. The term referred to is  $e^{-E/RT}$ , where  $E$  is the critical increment per gram-molecule,  $R$  the gas constant per gram-molecule, and  $T$  the absolute temperature. It is this quantity that governs the magnitude of the temperature coefficient of a reaction, and, as is evident, the greater the value of  $E$  the greater is the temperature coefficient.

Let us suppose that a given reaction occurs in a homogeneous system, the sum of the critical increments of the reactants being  $E_1$ , whilst the sum of the critical increments for the same reaction when a heterogeneous catalyst is present is  $E_2$ . Then  $E_1 > E_2$ . The ratio of the velocity constant in the presence of the catalyst to that when the catalyst is absent is given essentially by the ratio  $e^{-E_2/RT}/e^{-E_1/RT}$  or  $e^{(E_1-E_2)/RT}$ . This is, in general, a large positive quantity; it may be referred to as the catalytic factor. Let us suppose that the process considered involves the dissociation of a gaseous molecule. If this occurs in the homogeneous phase, the critical increment is large, of the order of 50,000 to 100,000 calories per gram-molecule. This energy has to be supplied by absorption of the radiation present in the system, and the greater the amount of energy required the higher must be the temperature in order that a sufficient number of quanta of high frequency may be available. If, on the other hand, a catalyst is present which is capable of condensing or adsorbing the gas in the atomic form, then the energy required is essentially that of sublimation or desorption of the atomic resultants from the surface diminished by the energy of adsorption or condensation of the molecular reactant. Such effects are in general small, of the order 5000 to 10,000 calories per gram-molecule. Hence in this case the catalytic factor would be  $e^{(50,000-5000)/RT}$ , which for the temperature  $T=1000^\circ$  would correspond with  $e^{22.5}$ , or  $10^{10}$  approximately. It is evident that the effect which we have been considering is of very great magnitude, and to this extent is in agreement with the known high efficiency

of heterogeneous catalysts. From the point of view of the energy changes involved, therefore, the action of a catalyst is to be ascribed to the substitution of relatively small energy terms of the nature of de-sorption or sublimation effects in place of true critical energies of activation or dissociation. In general, the problem is not so simple as the case just considered. Frequently more than one reactant is involved, and in some cases partial activation or polarisation of one or more of the reactants may be effected without such reactant coming into direct contact with the surface of the solid itself. This will naturally occur when the surface is already covered by a reactant which possesses high capacity of adsorption. In general, however, the function of the catalyst is to bring at least one of the reactants into the active form, which would otherwise only be attained in the homogeneous phase by exceedingly high temperature conditions. The possibilities which present themselves will be rendered somewhat clearer by a preliminary examination of one or two actual cases.

#### *The Reaction between Oxygen and Sulphur.*

We shall first of all consider the reaction,  $S + O_3 = SO_2$ , as occurring in the homogeneous gaseous state.

Since the resultant contains two atoms of oxygen, the process does not require complete dissociation of the oxygen molecule as a preliminary step. Instead, a partial activation or polarisation of the oxygen molecule is sufficient. A value for this quantity may be obtained from a consideration of the thermal decomposition of ozone, which has been measured by Chapman and Jones (T., 1910, 97, 2463), the reaction being shown to be bimolecular. The details of the calculation will be given in a subsequent paper, but it may be stated here that the critical increment of ozone per gram-molecule, obtained from Chapman and Jones's results, is 10,690 cal. Further, the heat evolved at constant volume when two gram-molecules of ozone decompose into three gram-molecules of oxygen has been determined with accuracy by Kailan and Jahn (*Zeitsch. anorg. Chem.*, 1910, 68, 243), the value being 69,000 cal. Applying the quantum expression (compare T., 1917, 111, 1086) to the process  $2O_3 \rightarrow 3O_2$ , we obtain  $69,000 = 3E'_{O_2} - 21,380$ , whence  $E'_{O_2} = 30,127$  cal., or 30,000 cal. in round numbers. The symbol  $E'$  denotes the critical increment per gram-molecule required for the partial activation or polarisation of oxygen which will permit three molecules thus activated to react to form two molecules of ozone. A molecule possesses, in general, different degrees or stages of activation, and this may not be the one required in the case of

the union of oxygen with sulphur. All partial activations are, however, small quantities compared with the activation required to cause complete dissociation of a molecule. So far as order of magnitude is concerned, the above value may be employed in this preliminary investigation.

We have now to consider the activation of sulphur vapour. In the temperature range  $200^{\circ}$  to  $500^{\circ}$ , the vapour of sulphur consists mainly of the molecular form  $S_8$ . Preuner and Schupp (*Zeitsch. physikal. Chem.*, 1909, **68**, 148) have measured the equilibrium of the reaction  $4S_8 = 3S_2$ . The mean value of the heat effect is 26,500 cal. This heat is absorbed in breaking down  $3S_8$  molecules to  $4S_2$  molecules. The same authors have obtained a fairly accurate value for the heat absorbed, namely, 58,000 cal., in the gaseous reaction  $S_8 = 3S_2$ . Hence the process  $\frac{1}{4}S_8 \rightarrow S_2$  requires an absorption of heat equal to 21,542 cal. We have now to consider the heat absorbed in the dissociation of  $S_2$  into the atomic state. Budde (*Zeitsch. anorg. Chem.*, 1900, **78**, 169) has measured, by an explosion method, the equilibrium of the reaction  $S_2 = 2S$ , in the gaseous state, over the temperature range  $2000^{\circ}$  to  $2500^{\circ}$ . The results do not lead to an accurate value for the heat effect. Budde takes the value 120,000 cal. per gram-molecule. Von Wartenberg (*Zeitsch. anorg. Chem.*, 1908, **56**, 320) estimates the heat effect to be 90,000 cal. approximately. It has been shown (compare T., 1918, **113**, 471) that the critical increment in the case of the dissociation of a molecule into atoms is connected with the heat absorbed by the relation  $-Q_v = E - \frac{1}{2}RT$ . At  $T = 2000^{\circ}$ , the value of  $E$  obtained from Budde's results is therefore 122,000 cal., but this is liable to considerable error. On the radiation hypothesis, this energy should be given by  $Nh\nu$ , where  $\nu$  is the frequency of the light absorbed,  $N$  the number of molecules in one gram-molecule, and  $h$  Planck's constant. Martens (*Ann. Physik*, 1902, [iv], **8**, 603) has calculated that sulphur should possess a band in the ultra-violet region at  $\lambda = 226 \mu\mu$ . The corresponding frequency is  $13.3 \times 10^{14}$ , and therefore  $Nh\nu$ , or the critical increment per gram-molecule, should be 125,550 cal. This is remarkably close to the value calculated from Budde's data. In fact, the agreement is partly accidental. It is probable that the value obtained from Martens's data is the more correct. It follows that the heat of dissociation of diatomic sulphur into the atomic state in a gaseous system is 123,000 cal. per gram-molecule. Hence the energy absorbed in the process  $\frac{1}{4}S_8 \rightarrow 2S$  is  $(123,000 + 21,540)$ , or 144,500 cal. in round numbers. As might be expected, the chief factor in the total energy change from  $S_8$  to atomic sulphur is the single process of dissociating the  $S_2$  molecules. The critical increment

required to produce two gram-atoms of sulphur in the gaseous state from the corresponding quantity of  $S_8$  molecules is 147,000 cals., and therefore the critical increment per gram-atom is 73,500 cals.

We have now to consider the formation of sulphur dioxide from oxygen and sulphur, the latter consisting of  $S_8$  molecules, the system being entirely gaseous. The partial critical increment of the oxygen is taken to be 30,000 cals. per gram-molecule. Hence the total critical increment of the system ( $S + O_2$ ) under the conditions stated is  $(73,500 + 30,000)$ , or 103,500 cals. The heat of formation of sulphur dioxide from solid sulphur and gaseous oxygen is 69,400 cals. per gram-molecule (Berthelot) (compare Ferguson, *Proc. Nat. Acad. Sci.*, 1917, **3**, 371). The heat of vaporisation of sulphur is 12,000 cals. per gram-atom in round numbers. Hence the heat of formation of sulphur dioxide from its gaseous components is 81,400 cals. Employing the relation:

$$\text{Heat evolved} = E_{\text{resultants}} - E_{\text{reactants}}$$

we get  $81,400 = E_{SO} - 103,500$ , whence  $E_{SO} = 184,900$  cals. per gram-molecule. It follows from this value that the frequency of the effective radiation is  $19.6 \times 10^{14}$ , and the wave-length  $\lambda = 153 \mu\mu$ . Sulphur dioxide is known to have an absorption band in the extreme ultra-violet region beyond  $200 \mu\mu$  (compare Garrett, *Phil. Mag.*, 1916, [vi], **31**, 505), but the position of the band has not as yet been located.

The above exceedingly high value for the critical increment of sulphur dioxide requires that the molecule should be correspondingly stable. Thus it should not be possible to decompose it into its components by a quartz mercury lamp, since quartz does not transmit wave-lengths longer than about  $185 \mu\mu$ . As an illustration of its stability, it may be mentioned that von Wartenberg (*loc. cit.*) was unable to detect any sensible dissociation of sulphur dioxide even at  $2200^\circ$  abs. For our present purpose, it is more important to observe that the critical increment of the reactants ( $S + O_2$ ) is also very high, namely, 103,500 cals.

The numerical values given above refer to the reaction non-catalysed. If, however, the reaction is carried out in the presence of solid or fused sulphur, heterogeneous catalytic effects enter. This has been shown experimentally by Bodenstein and Caro (*Zeitsch. physikal. Chem.*, 1910, **75**, 30), the sulphur acting as a positive catalyst. The result of the positive catalysis is that the critical increment of the system ( $S + O_2$ ) is much less than the value given above. From the temperature coefficient obtained by Bodenstein and Caro in the region of  $250^\circ$ , in the presence of solid sulphur, it is found that the critical increment of the reactants

(S + O<sub>2</sub>) lies between the limits 31,308 and 34,184 cals., the mean value being 33,000 cals. in round numbers.

It is possible to account approximately for the order of magnitude of the critical increment obtained, when heterogeneous catalysis occurs, by supposing that the oxygen is already activated at the temperature chosen before coming into contact with the sulphur surface, the increment of partial activation of oxygen being of the order 30,000 cals., as we have seen already. The sulphur itself is already in the atomic state in the surface layer of the solid, and consequently does not require further activation. The heat of volatilisation of the sulphur dioxide per gram-molecule is a quantity of the order 5000 cals., so that in all the apparent increment is of the order 35,000 cals., which agrees moderately well with that observed.

In the above case, the catalytic factor at 250° is  $e^{(103,500 - 35,500)/RT}$  or  $e^{68,000/RT}$ , or 10<sup>28</sup> approximately. These numbers are simply employed for purposes of illustration; sufficient data have not yet been accumulated to permit of more exact calculation.

If such changes in the critical increment are brought about as a result of catalytic effects, it is necessary to conclude that in general the heat effect of a process will be modified by the catalyst, and if this is the case the variation of the equilibrium constant of the reaction in the surface layer with temperature will be affected, so that finally the equilibrium constant of the catalysed reaction will differ from that of the non-catalysed reaction. This conclusion is in general agreement with that arrived at by Bancroft (*J. Physical Chem.*, 1917, **21**, 573) on false equilibria and the effect of heterogeneous catalysis on the position of the equilibrium.

#### *The Union of Oxygen and Hydrogen.*

Bodenstein (*Zeitsch. physikal. Chem.*, 1899, **29**, 665) has found that the temperature of the termolecular velocity constant, corresponding with the reaction  $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ , is 1.75 for 10° over the temperature range 482° to 509°. The reaction proceeds under the conditions employed almost entirely at the surface of the porcelain containing-vessel. From the above value of the temperature coefficient, it would follow that the critical increment for two gram-molecules of hydrogen and one gram-molecule of oxygen is 66,000 cals., and therefore for one gram-molecule of hydrogen and one half-gram-molecule of oxygen the increment of the reactants is 33,000 cals. Bodenstein's results have, however, been criticised by Bone and Wheeler (*Phil. Trans.*, 1906, [4], **206**, 1), who find that the reaction is not termolecular, but approximately unimole-

cular, especially unimolecular with respect to the hydrogen. The reaction which appears to occur is therefore  $H_2 + O = H_2O$ . Bone and Wheeler have given data for the reaction from which the temperature coefficient and critical increment of the reactants may be calculated when nickel is the catalyst. For the temperature range  $473^\circ$  to  $493^\circ$  abs., the critical increment of the reactants is calculated to be 35,000 cals., which agrees fairly well with the value obtained from Bodenstein's results for the porcelain surface. Over the temperature range  $493^\circ$  to  $513^\circ$  abs., the results obtained by Bone and Wheeler give an increment of 52,000 cals. in round numbers. This is considerably greater than that obtained at the lower range of temperature, and indicates that the catalytic effect is relatively less efficient at the higher temperature, due, presumably, to diminished adsorption of the reactants. In both cases, however, the increment is a relatively small quantity, very much smaller than would be expected from the process occurring in the homogeneous phase, for the molecule of oxygen, which has to be dissociated, is very stable.

We have now to attempt to account for a quantity of the above order of magnitude on the basis of the energy-mechanism outlined. Let us assume, in the first place, that the oxygen is adsorbed and exists in the atomic state attached to certain positions on the surface of the catalyst. It is necessary that an activated or polarised molecule of hydrogen shall come into contact with an oxygen atom. It is only necessary for the hydrogen to be partly activated. Bohr (*Phil. Mag.*, 1913, [vi], 26, 1, 476, 857) has investigated the energy changes which occur in the molecule and the atom of hydrogen in various processes involving the removal and addition of an electron. Bohr has calculated that the process of transferring an electron so as to give rise to a system consisting of a positively charged hydrogen atom and a negatively charged one requires an absorption of energy of 21,000 cals. per gram-molecule of hydrogen. We shall employ this value in the present case, although there is evidence that a somewhat higher value is probably more correct. The latent heat of vaporisation of water is in round numbers 9000 cals. per gram-molecule in the neighbourhood of  $100^\circ$ . As before, we shall assume that the heat of desorption of the water produced in the reaction is of the same order of magnitude. Hence we would expect the critical increment of the process to be of the order 30,000 cals. per gram-molecule of hydrogen and per gram-atom of oxygen. This agrees moderately with the observed value.

Sufficiently accurate data are not as yet available for calculating the critical increment of the reactants of the same reaction in the

homogeneous gaseous state. It is necessary to dissociate the molecule of oxygen, and this appears to require a quantum of energy corresponding with approximately the region  $\lambda = 200 \mu\mu$ , whence the critical increment per gram-molecule is of the order 140,000 to 150,000 cals. That is, the total increment of the reactants, reckoned per gram-molecule of hydrogen, is  $21,000 + 140,000/2$ , or 91,000 cals. The catalytic efficiency is therefore given by the ratio  $e^{-33,000/RT}/e^{-91,000/RT}$  or  $e^{58,000/RT}$ . At  $500^\circ$  this factor is of the order  $10^{17}$ . These figures are merely illustrative, but they serve to indicate the great influence on the velocity which is to be expected on the basis of the treatment suggested.

In dealing with the union of oxygen and hydrogen, it has been assumed above that the oxygen is condensed in the atomic form on the catalyst, the subsequent chemical change being  $H_2 + O = H_2O$ . From a number of observations made by Bone and Wheeler (*loc. cit.*), it appears that hydrogen is preferentially adsorbed. In such cases, the most probable reaction, because it involves the minimal critical increment, would be represented by  $H_2 + O_2 = H_2O_2$ , in which the hydrogen and oxygen are partly activated, but neither of them is completely dissociated. The formation of water would result from the subsequent decomposition of the hydrogen peroxide. The idea that hydrogen peroxide is an intermediate stage is, of course, not new. It appears from such considerations that the specific nature of the catalyst may determine the actual mechanism of a given reaction to a large extent.

#### *The Union of Oxygen and Silicon.*

In the reactions just considered, the critical increment of partial activation of oxygen has been taken to be 30,000 cals. approximately, this being the value required for the formation of ozone. As already pointed out, more than one stage of activation may be anticipated up to the limiting activation which corresponds with complete dissociation of the molecule into atoms. Each activation corresponds with a certain size of quantum of radiant energy, that is, with a certain frequency. The general conclusion reached in connexion with absorption spectra is that frequencies are related to one another in terms of even multiples of some fundamental frequency, that is, various degrees of activation are similarly related. A low degree of activation of the oxygen molecule requires 30,000 cals. of energy to be absorbed per gram-molecule, and therefore higher degrees of activation would require 60,000, 90,000 cals., etc., up to the limiting value of complete dissociation, which



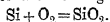
appears to correspond with a quantity of the order 140,000 to 150,000 cals.

Sufficient information is not as yet available to enable us to say how many of these possible degrees of activation may actually manifest themselves. As an example of partial activation of oxygen which is apparently considerably greater than 30,000 cals., we may take the case of the formation and decomposition of an exceedingly stable compound, silica or quartz.

To decompose a molecule of quartz, it is evident that a quantum in the very extreme ultra-violet portion of the spectrum is required, in order to supply the necessary energy. It is well known that quartz commences to absorb radiation sensibly beyond the wave-length  $185\ \mu\mu$ . S. Richardson (*Phil. Mag.*, 1916, [vi], **31**, 463) finds that the dispersional wave-length of quartz is  $105\ \mu\mu$ . It does not necessarily follow that the dispersional wave-length or frequency is that required for complete dissociation of the molecule. That in the case of quartz, however, the necessary wave-length cannot differ much from  $105\ \mu\mu$  is rendered probable by the following consideration. In a quartz mercury vapour lamp, it is generally believed that the quartz remains undecomposed; otherwise it would be difficult to account for the life and permanence of the lamp. That is, quartz can only be decomposed by a wave-length which is shorter than any emitted by the mercury vapour. O. W. Richardson and Bazzoni (*Phil. Mag.*, 1917, [vi], **34**, 285) have found that there is a limiting wave-length in the spectrum of a substance; that is, no wave-length shorter than a certain value, characteristic of the substance, can be emitted. In the case of mercury vapour, this limiting wave-length lies between 120 and  $100\ \mu\mu$ . The mean of these two limits is  $110\ \mu\mu$ , and we conclude on the above reasoning that quartz can only be decomposed by a wave-length shorter than this value. This points fairly definitely to S. Richardson's value,  $105\ \mu\mu$ , for the dispersional wave-length of quartz as being the wave-length capable of decomposing the molecule.

The critical increment corresponding with  $\lambda=105\ \mu\mu$  is 270,000 cals. per gram-molecule of quartz, an enormous quantity, which is in qualitative agreement with the known stability of quartz.

We have now to consider the heterogeneous reaction



On Langmuir's view as applied in the present paper, we regard the silicon as already in the atomic state. If  $x$  is the necessary critical increment of oxygen per gram-molecule, then  $x$  is likewise the total critical increment of the reactants. The heat of the reaction is known to be 184,000 cals. in round numbers, and hence,

on applying the quantum-heat expression: heat evolved = critical increment of resultants - critical increment of reactants, we obtain  $184,000 = 270,000 - x$ , whence  $x = 86,000$  cals. Owing to the error in the observed heat effect and in the value of the critical increment of quartz, this value for the critical increment of oxygen may be regarded as agreeing approximately with the value 90,000 cals. expected from the lower degree of activation of the molecule. What is particularly important is that even this value does not correspond with complete dissociation of the oxygen molecule. We may therefore conclude that the molecule of quartz possesses the structure  $\text{Si} \begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix}$ , rather than  $\text{O}:\text{Si}:\text{O}$ . This is an illustration of how a knowledge of the necessary critical increments—which in the present case, unfortunately, are not known with precision—may lead to information concerning molecular structure.

One of the chief difficulties met with in the kinetics of heterogeneous reactions has its origin in the selective nature of the absorbability of the reactants and the resultants, particularly the latter. The so-called catalytic "poisons" are now generally regarded as owing their effect to marked selective adsorption, as a result of which the surface of the catalyst becomes covered with a layer of molecules, and is thus no longer capable of catalysing the reaction. In many cases, the resultants of the reaction are adsorbed in this manner, and consequently function as a catalytic poison. Since the extent of adsorption diminishes as the temperature rises, it is obvious that when such poisoning effects are present the temperature coefficient of the reaction velocity over a certain range of temperature is not comparable with that over a different range, for the total observed velocity depends not only on the true effect of temperature on the chemical process itself, but likewise on the alteration in the extent of active surface presented to the reactants. The simplest conditions are obviously those in which the adsorption effects are a minimum, and such conditions will occur generally when the energy required for sublimation or desorption is small. In the other cases where adsorption effects are large, it is necessary to correct the observed velocity constants for the change in the area of the effective surface produced as a result of the change in temperature. Thus in the case in which the resultant is markedly adsorbed, and therefore acts as a negative catalyst, the temperature coefficient will possess too high a value, and instead of decreasing as temperature rises, may even increase. A similar abnormal behaviour is to be anticipated when a reaction proceeds partly in the homogeneous gaseous phase, partly in the

surface, for as the temperature rises the reaction tends to predominate in the gaseous phase, and therefore possesses a higher temperature coefficient.

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## XXII.—*The Estimation of the Methoxyl Group.*

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SINCE the introduction of the Zeisel method for the estimation of methoxyl groups (*Monatsh.*, 1885, **6**, 989; 1886, **7**, 406; Benedikt and Grüssner, *Chem. Zeit.*, 1889, **13**, 872), numerous attempts have been made to simplify the apparatus and shorten the operation. The method of rectifying the methyl iodide proposed by Zeisel is effective but troublesome; the inclined condenser has to be of considerable length, and consequently occupies some bench space, whilst the constant supply of water to the condenser at about 50° necessitates supervision. A further inconvenience of the Zeisel method is the trouble experienced in working up the precipitate of double iodide and nitrate of silver, time being lost in evaporating the alcohol and obtaining the silver iodide in a pure condition.

The use of a rectifying column provided with a thermometer, in place of the inclined condenser fed with water at an approximately definite temperature, was recommended by Hewitt and Moore (*T.*, 1902, **81**, 318), and impurities in the hydriodic acid were removed by passing carbon dioxide through the acid at 130° before introducing the substance under examination. Considerable saving in bench space was effected, and during the operation it was only necessary to control the stream of carbon dioxide and the flame under the glycerol bath so as to give the necessary temperatures in the reaction flask and at the top of the rectifying column. Several modifications of the Zeisel method have been suggested in which ordinary rectification has been relied on in place of inclined condensers in which the temperature is controlled by running water (Perkin, *T.*, 1903, **83**, 1367; Zeisel and Fanto, *Zeitsch. anal. Chem.*, 1903, **42**, 549; Stritar, *ibid.*, 579; Hesse, *Ber.*, 1906, **39**, 1142). Shortening the process by estimation of the methyl iodide in a more rapid manner was left untouched for years. The necessity of estimating methyl iodide obtained from methyl alcohol

mixtures rapidly and accurately caused the present authors to search for a quick process.

Since combination of alkyl iodides with bases of the pyridine series takes place very rapidly, there seemed to be a promising way of obtaining the iodide in an ionisable form and then estimating it volumetrically. After working out a satisfactory process, it was found that the same fundamental idea of combining the methyl iodide with a tertiary base had already been utilised (Kirpal and Bühn, *Ber.*, 1914, **47**, 1084), but the subsequent volumetric estimation of iodide by standard silver nitrate solution may be considerably shortened. Instead of rejecting the excess of pyridine by evaporation and estimating the iodide with standard silver nitrate, using a chromate as indicator, the pyridine and its methiodide may be directly diluted with water, acidified with nitric acid, a known amount of silver nitrate added, and the excess of the latter determined by thiocyanate according to Volhard's method. Adoption of this procedure reduces the time of experiment considerably.

The applicability of Volhard's method to the estimation of methyl iodide after reaction with pyridine was controlled in a separate experiment. 3.10 Grams of freshly distilled methyl iodide were diluted to a volume of 100 c.c. with pyridine which had been saturated with carbon dioxide. By dilution with water, addition of silver nitrate, and determination of the excess of silver with thiocyanate, 3.13 grams of methyl iodide per 100 c.c. were found.

#### *Method.*

*Hydriodic Acid.*—The hydriodic acid is prepared by saturating an aqueous suspension of iodine with hydrogen sulphide, distilling the resulting solution, and collecting the fraction boiling between 123° and 127° (D 1.7) for use.

Residues from analyses are redistilled and used again.

*Pyridine.*—Complete separation from picoline is unnecessary; it is, however, advisable to remove substances of high boiling point.

Pyridine bases as obtained from tar distillers are mixed with two-thirds of their weight of water and fractionated. The fraction distilling between 93° and 97°, containing the mixture of constant boiling point, is shaken with one-third of its weight of solid sodium hydroxide, the upper layer is separated, fractionally distilled, and the bases distilling between 114° and 117° are collected for use. Residues containing pyridine may be accumulated, rendered alkaline with one-fiftieth of their weight of solid sodium hydroxide, distilled, the distillate at 93—97° collected, and worked up.

*The Estimation.*—The apparatus consists of the usual carbon dioxide generator, decomposition flask heated in a glycerol bath to 130°, and rectifying column (four-pear or other suitable form). The carbon dioxide carrying the methyl iodide vapour is passed through two test-tubes in series, each containing 10 c.c. of pyridine.

For the estimation, a suitable weight of the substance is taken, and 20 c.c. of hydriodic acid (D 1·7) are added.

After the experiment has been in progress for one hour, the contents of the test-tubes are completely washed into a graduated flask, when they are diluted with water, and the iodide is estimated by the process indicated above.

In all cases, early in the course of the experiment, a yellow coloration develops in the pyridine. This vanishes on diluting the pyridine at the end of the experiment. Its appearance, therefore, need cause no apprehension to the analyst that free iodine is finding its way into the pyridine. Moreover, carefully purified samples of methyl iodide and pyridine on admixture develop colour. The behaviour of a mixture on dilution with water was compared with that of an iodine solution of equal depth of colour. On diluting a 3 per cent. solution of methyl iodide in pyridine with a quarter of its volume of water, the colour became very pale, and with its own volume of water it almost vanished. The iodine solution, on being similarly diluted, still retained its colour. It would thus appear that the coloration is not due to free iodine. Should, however, the colour persist on dilution with water, it is then advisable to discharge it with thiosulphate solution.

### Analyses.

Substance.	Percentage of methoxyl group	
	Found.	Calculated.
Brucine hydrate .....	13·5	13·3
Methyl oxalate .....	50·1	52·5
Methyl alcohol .....	95·2	96·9
"    " .....	95·2	96·9
"    " .....	96·0	96·9
"    " .....	96·3	96·9
Methyl salicylate .....	19·7	20·4

A methylated cellulose which gave 39·1 per cent. of methoxyl by the gravimetric Zeisel method was found to contain 39·2 per cent. by the present method.

Unsatisfactory results were obtained with a sample of methyl benzoate and with one of hydrated quinine sulphate.

This comparatively rapid method for the estimation of methoxyl

groups may be applied conveniently to the products of wood distillation or other mixtures containing methyl alcohol.

Methyl alcohol has usually been estimated in these products by conversion into methyl iodide, and measurement of the volume of the latter compound (Krell, *Ber.*, 1873, 6, 1310; Grodzky and Krämer, *ibid.*, 1492). Zeisel and Stritar's process of weighing volatilised iodine as silver iodide obviates the inexactness due to determination of the volume of the methyl iodide, but time may be saved by combining the methyl iodide with a tertiary base and estimating the iodine volumetrically.

A suitable amount (see below) of the liquid to be analysed is heated with 20 c.c. of hydriodic acid (D 1.7) for one hour. The contents of the test-tubes are then completely washed into a graduated flask and made up with water to 100 c.c. An aliquot portion (see below) of the diluted solution is introduced into a glass stoppered bottle of 250 c.c. capacity, 70 c.c. of water are added, and then, in order, 25 c.c. of *N*/10-silver nitrate solution and 30 c.c. of approximately 10*N*-nitric acid. The bottle is well shaken by hand for five minutes, and 5 c.c. of concentrated ferric alum indicator are added. *N*/10-Thiocyanate solution is now run in until further addition of one drop imparts a permanent orange colour to the liquid.

Suitable amounts of liquids to be taken for analysis are given below.

*a* represents the volume of material to be operated on and its dilution when necessary.

*b* gives the volume of the diluted aqueous pyridine solution, obtained as described above, to be actually used in a titration.

*c* is the formula to be used giving the weight in grams of methyl alcohol in 100 c.c. of the liquor analysed, where *t* is the number of c.c. of *N*/10-thiocyanate solution used in the titration. (*Note*.—The figure 25 given in the formulæ must be multiplied by *f*, the factor for the silver nitrate solution, if this is not exactly decinormal.)

*Pyroligneous Acid*.—(*a*) Take 5 c.c. of the original liquor; (*b*) 40 c.c.; (*c*)  $0.16 (25 - t)$ .

*Crude Wood Naphtha*.—(*a*) Take 10 c.c., dilute to 100 c.c. with water, and use 5 c.c. of the diluted solution for distillation with hydriodic acid; (*b*) 40 c.c.; (*c*)  $1.6 (25 - t)$ .

*Methyl Alcohol and Mixtures of the Alcohol with Acetone*.—(*a*) Take 10 c.c., dilute to 100 c.c. with water, and use 5 c.c. of this diluted solution for the estimation; (*b*) 20 c.c.; (*c*)  $3.2 (25 - t)$ .

*Analyses.*

Artificial mixtures containing methyl alcohol and other products of wood distillation were made up and analysed by the method described.

Liquor Number.	Composition. No. of grams of methyl alcohol per 100 c.c. of liquor.	
	Actual.	Found.
1 .....	2.39	2.35
2 .....	68.5	68.1
3 .....	2.39	2.35
4 .....	31.8	31.5

Analyses of purified methyl alcohol by the present method have already been given.

It will be seen that, on an average, the results are 1 per cent. too low. Stritar and Zeidler (*Zeitsch. anal. Chem.*, 1904, **63**, 387) found that the maximum amount of methyl iodide obtainable from pure methyl alcohol in a Zeisel estimation corresponded with a 99 per cent. yield.

Liquors 1 and 2 were aqueous solutions of purified methyl alcohol. Liquor 3 contained, per 100 c.c., 7.03 grams of acetic acid, 0.80 gram of acetone, and 2.39 grams of methyl alcohol, the remainder being water. It represented a pyroligneous acid. Liquor 4 was an equilibrium mixture prepared from 10.04 grams of acetic acid, 39.60 grams of acetone, and 31.82 grams of methyl alcohol, made up to 100 c.c. with water (1.27 grams). This mixture, which, of course, contained methyl acetate, represented the first runnings obtained in the rectification of crude wood naphtha.

*Compounds yielding Methyl Iodide, other than Methyl Alcohol,  
present in Wood Distillates.*

The constituents of wood distillates have been examined by Stritar and Zeidler (*loc. cit.*) with a view to determine which yield methyl iodide on treatment with hydriodic acid. They found that acetone gave no methyl iodide, whilst the yield from both formaldehyde and acetaldehyde was negligible. Methyl acetate gave one equivalent of methyl iodide, and methylal and dimethylacetal each gave two. Allyl alcohol yielded its equivalent of *sec.*-propyl iodide. Guaiacol and other methyl derivatives of the phenols yielded their equivalent of methyl iodide.

Of these substances, the quantities of acetal encountered are too

small to be of consequence. According to Grodzki and Krämer (*loc. cit.*), the amounts of allyl alcohol and of methyl alcohol in raw wood spirit are in the ratio of 2 to 1000. Stritar and Zeidler find that guaiacol may be eliminated from aqueous solutions of crude wood spirit by shaking with animal charcoal. They state that on omitting this treatment, the amount of methyl alcohol found is too high by about 2 parts in 100 parts. It will be seen that the quantities of alkyl iodide yielded by the amounts of allyl alcohol and of guaiacol present in the aqueous wood distillates, relatively to that yielded by the methyl alcohol present, border closely on the experimental error. It is the experience of the authors that, where precautions are taken to eliminate these substances preliminary to analysis, the errors due to losses outweigh the error introduced through ignoring their presence.

The present method gives the total methyl alcohol, including both the free alcohol and that which is combined as methyl acetate. If it is desired, the amount of ester present may be determined by quantitative hydrolysis.

The alcoholic silver nitrate of the Zeisel method of estimating methoxyl may be replaced by pyridine. The pyridinium methyl iodide formed can be determined by Volhard's thiocyanate method.

Methyl alcohol in wood distillates may be determined by the method described above.

[Received, January 17th, 1919.]

### XXIII.—*The Preparation of Monomethylaniline.*

By PERCY FARADAY FRANKLAND, FREDERICK CHALLENGER, and  
NOEL ALBERT NICHOLLS.

WHEN aniline is submitted to the action of the usual methylating agents, it is difficult to limit the course of the reaction to the introduction of a single methyl group. We have investigated the production of monomethylaniline by three methods, with a view to obtain it in a pure condition.

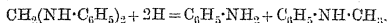
(1) The process described in the German Patent 75854, and with slight modifications in the French Patent 212506, consists in condensing aniline with formaldehyde and then reducing with zinc dust and concentrated aqueous sodium hydroxide until a test portion dissolves to a clear solution in acetic acid. Any unreduced methyleneaniline,  $\text{CH}_2\text{:N}\cdot\text{C}_6\text{H}_5$ , is thereby converted into insoluble



anhydroformaldehydeaniline,  $(\text{CH}_2\cdot\text{N}\cdot\text{C}_6\text{H}_5)_3$ . Using 100 grams of aniline, we have found the reduction to be completed in twelve to fifteen hours, and have obtained about 55 per cent. of the theoretical yield of methylaniline. The Patent Specifications make no mention of the yields obtained.

The principal advantage of this method lies in the fact that the product, although rich in aniline, contains only traces of dimethylaniline. The presence of the aniline may be the result of incomplete condensation with formaldehyde in the first instance, or of the hydrolysis of the methyleneaniline by the hot water, or of both causes. The primary base can be recovered in the form of its zincchloride, which is almost insoluble in water, the methylated bases not being affected by this reagent (*Monatsh.*, 1888, **9**, 514). The method appears to work very satisfactorily.

Morgan (English Patent 102834), who has also studied the reduction of methyleneaniline, suggests that the poor yield of methylaniline may be due, in addition to hydrolysis, to the conversion of some of the methyleneaniline into *s*-diphenylmethylenediamine,  $\text{CH}_2(\text{NH}\cdot\text{C}_6\text{H}_5)_2$ , and anhydroformaldehydeaniline. We have failed to obtain more than traces of monomethylaniline from the last-named substance (compare, however, Goldschmidt, *Chem. Zeit.*, 1904, **28**, 1229), but when *s*-diphenylmethylenediamine (Eberhardt and Welter, *Ber.*, 1894, **27**, 1804; Eibner, *Annalen*, 1898, **302**, 349) is reduced with zinc dust and alkali hydroxide under the conditions of the earlier patents, aniline and monomethylaniline are produced in equal amounts, probably according to the equation



We attempted to diminish the hydrolysis by performing the reduction in concentrated alcoholic solution. The yield of methylaniline was, however, only about 46 per cent. No better results were obtained by increasing the quantity of formaldehyde; 1·5 molecular proportions gave rise to some dimethylaniline, whilst with 10 molecular proportions, considerable quantities of this base were formed.\*

This appears to be due to the interaction of monomethylaniline and formaldehyde, giving rise to *s*-diphenyldimethylmethylenediamine, which then undergoes reduction. This reaction would, moreover, be analogous to the reduction of *s*-diphenylmethylenediamine. The condensation product of formaldehyde and methyl-

\* Compare the action of formaldehyde on methylaniline in acid solution (Goldschmidt, *loc. cit.*) and on methyl-*o*-toluidine (Braun, *Ber.*, 1908, **41**, 2153), also on ammonium chloride (Werner, *T.*, 1917, **112**, 844). See also Pinnow, *Ber.*, 1894, **27**, 3166; Cohn, *Chem. Zeit.*, 1900, **24**, 564.

aniline (Braun, *Ber.*, 1908, 41, 2147) was therefore prepared and reduced under the usual conditions, with the result that much dimethylaniline was produced.

(2) The process described in various works of reference consists in heating aniline hydrochloride with methyl alcohol in an autoclave to 180—200°.\* The best result obtained by us in a series of thirteen experiments was a 55 per cent. yield of monomethylaniline. Experiments in sealed tubes confirmed these results.

We have also investigated a variation of the above method, in which aniline hydrochloride and methyl alcohol are heated together in the presence of glacial acetic acid (*Ber.*, 1897, 30, 3072). The most favourable result was a yield of 56 per cent. of methylaniline.

(3) The demethylation of dimethylaniline by heating with aniline hydrochloride at above 180°. In the most favourable experiments, a yield of 55 per cent. of methylaniline was obtained. Aniline was also heated to a high temperature with dimethylaniline hydrochloride with similar results, but it was found necessary to heat for a much longer period. This was probably due to the more basic nature of dimethylaniline. A condition of equilibrium between the three bases and hydrochloric acid would appear to be established.

At the time these experiments on demethylation were performed (1916), we were unable to find any record of similar work on this subject, apart from the well-known phenomenon of the transfer at above 300° of alkyl groups from nitrogen to the ring.

According to Schultz ("Chemie des Steinkohlentheers," 1900, 3rd ed., I, p. 98), monoethylaniline may be prepared by heating aniline hydrochloride with diethylaniline. No yields or references to the original literature are given, but the reaction is obviously not quantitative, since it is stated that the hydrochloride of diethylaniline remains in solution.

#### EXPERIMENTAL.

*Preparation of Monomethylaniline according to D.R.-P. 75854.*

*Materials Used.*—One hundred grams of aniline, 80.5 grams of formaldehyde (37 per cent.), 30 grams of methyl alcohol, 25 grams of sodium hydroxide solution (D 1.38), 150 grams of zinc dust, 1 litre of water, and 225 grams of sodium hydroxide solution.

\* The published statements concerning the yields of monomethylaniline obtained in this way are very contradictory. See Wahl-Atack, "Organic Dyestuffs," p. 70; Cain, "Intermediate Products," p. 61; Lunge, "Chem. Techn. Untersuchungsmethoden," Vol. III, p. 761; Friedländer, "Fortschritte der Teerfarbenfabrikation," 1877—1887, p. 6.

The first four ingredients were mixed in a wide-mouthed bottle fitted with a stirrer and a reflux condenser, the zinc dust and water then added, and the temperature raised to about  $90^{\circ}$ . The remainder of the sodium hydroxide solution was gradually introduced and the stirring continued at this temperature until, after about twelve to fifteen hours, the methyleneaniline had disappeared. The bases were then distilled in a current of steam, extracted with ether, and a portion converted into the nitrosoamine. Yield of bases, 102 grams. Theory = 115 grams.

Thirty grams of the mixture gave 23 grams of dry phenylmethyl-nitrosoamine, whence the total yield of monomethylaniline is 54.5 per cent. of the theoretical.

*Preparation of Monomethylaniline according to French Patent*  
212506.

In these experiments, the quantities of material and method of procedure were as described above, with the exception that the whole of the sodium hydroxide solution was added at once.

In one case, where particularly efficient stirring was employed, the methyleneaniline had disappeared in six and a-half hours. In this experiment, the mixed bases contained 65 per cent. of monomethylaniline (by the nitrosoamine method of analysis), corresponding with a yield of 51.5 per cent. Other experiments with the same quantities and under similar conditions gave yields of 41.5 and 53.5 per cent. of the theoretical quantity of monomethylaniline.

*Reduction in the Presence of Excess of Formaldehyde.*

In two experiments on 100 grams of aniline, in which 0.5 molecular proportion of formaldehyde was used in excess, the yields of monomethylaniline were 46.5 and 55 per cent. In the first case, about 17 grams of the hydrochloride of *p*-nitrosodimethylaniline were obtained on nitrosification.

With an excess of 9 molecular proportions of formaldehyde, two experiments according to the German Patent gave scarcely any monomethylaniline; the reactions proceeded very slowly, and in one case much dimethylaniline was produced.

*Reduction in Concentrated Alcoholic Solution.*

One hundred grams of aniline, 25 grams of formaldehyde (36 per cent.), 840 grams of alcohol, 88 grams of solid sodium hydr-

oxide, 25 grams of aqueous sodium hydroxide (D 1.38), and 150 grams of zinc dust were vigorously stirred together. The reaction was complete in seven and a-half hours at about 60°, and the yield of methylaniline was 46.5 per cent. of the theoretical.

*Reduction of s-Diphenylmethylenediamine.*

Thirty grams of *s*-diphenylmethylenediamine, 125 grams of sodium hydroxide solution (D 1.38), 75 grams of zinc dust, 500 c.c. of water, and 25 grams of alcohol were mixed and vigorously stirred for ten and a-half hours at 70–90°. When a portion dissolved to a clear solution in dilute acetic acid (in which *s*-diphenylmethylenediamine is but sparingly soluble), the products were distilled in a current of steam.

Twenty-two grams of mixed bases were obtained, which gave 13 grams of phenylmethylnitrosoamine, corresponding with a yield of 10.2 grams of monomethylaniline. From the diazonium chloride solution, 10 grams of phenol were isolated, corresponding with 10 grams of aniline.

*Reduction of the Condensation Product of Formaldehyde and Monomethylaniline.*

Fifty grams of monomethylaniline, 19 grams of formaldehyde (36 per cent.), and 5–10 c.c. of aqueous sodium hydroxide were mixed, well shaken, and allowed to remain overnight.

The condensation product was separated by extraction with ether and reduced with a mixture of 150 grams of zinc dust, 1000 c.c. of water, 60 grams of methyl alcohol, and excess of sodium hydroxide solution at about 80°. After one and a-half days, the bases (44 grams) were removed by steam distillation. Nitrosification showed the product to contain 35 grams of monomethylaniline, whilst 9 grams of *p*-nitrosodimethylaniline hydrochloride were obtained.

*The Interaction of Aniline Hydrochloride and Methyl Alcohol in an Autoclave and in Sealed Tubes.*

In these experiments, the methylaniline was determined as the nitrosoamine and the aniline as phenol after decomposition of the diazonium salt. Dimethylaniline was separated and weighed as *p*-nitrosodimethylaniline hydrochloride, but as some of this always remained in solution, the figures for the tertiary base are low.

In experiment 8, aniline (140 grams) and sulphuric acid (16 grams) were used instead of aniline hydrochloride. Experiments 9—13 were made in sealed tubes, and in Nos. 11, 12, and 13 acetic acid (12 grams) was added.

Experi- ment.	Aniline hydro- chloride.	Methyl alcohol.	Tempera- ture.	Time in hours.	Percentage yield		
					Aniline.	Methyl- aniline.	Dimethyl- aniline.
1	110	32	180°	21 $\frac{1}{2}$	—	48.0	—
2	110	32	180	21 $\frac{1}{2}$	27.0	51.5	—
3	110	32	180	21 $\frac{1}{2}$	25.5	53.0	16.5
4	220	64	180	21 $\frac{1}{2}$	36.0	52.0	7.0
5	220	64	190	51 $\frac{1}{2}$	34.0	55.0	7.0
			above				
6	220	64	180	41 $\frac{1}{2}$	26.0	53.0	10.0
7	220	96	180	3	—	45.0	20.0
8	140	84	190	41 $\frac{1}{2}$	32.0	40.5	16.0
9	22	6.4	180	3	19.0	58.0	11.0
10	22	7.0	175	6	13.0	54.0	13.0
11	22	6.4	170	5	—	56.0	—
12	22	6.4	225	3	—	41.0	—
13	22	6.4	220	3	—	47.5	—

#### *Methylation of Aniline under other Conditions.*

(1) Twenty-six grams of aniline hydrochloride, 7 grams of methyl alcohol, and 25 c.c. of hydrochloric acid were heated in a sealed tube for six hours at 200—210°. Nitrosoamine=13.5 grams; yield of methylaniline=49.5 per cent.

(2) Thirty-six grams of aniline zincichloride and 6.4 grams of methyl alcohol were heated in a sealed tube for seven hours at 180°. Nitrosoamine=7.5 grams; yield of methylaniline=28 per cent.

(3) Twenty-two grams of aniline hydrochloride, 6.4 grams of methyl alcohol, and 15 grams of anhydrous calcium chloride were heated at 160° for three hours. Nitrosoamine=10 grams; yield of methylaniline=43 per cent.

(4 and 5). Twenty-eight grams of aniline (in the presence of 0.2 gram of iodine) were heated in one case with 10 grams, in another with 6.5 grams, of methyl alcohol for nine hours at about 220° (Knoll and Co., D.R.-P. 250236). In both cases, nitrosoamine=15 grams. Yield of methylaniline=42 per cent.

#### *The Demethylation of Dimethylaniline.*

*First Series.*—Interaction between aniline hydrochloride (13.0 grams) and dimethylaniline (12.0 grams) in molecular proportions in sealed tubes.

Experiment.	Temperature.	Time in hours.	Nitroso- amine.	Percentage yield of monomethylaniline
1	180°	6	12.5	46
2	200	6	15.0	55
3	220—235	5½	15.0	55

*Second Series.*—Interaction between dimethylaniline hydrochloride (31.5 grams) and aniline (18.6 grams) in molecular proportions in sealed tubes.\*

Experiment.	Temperature.	Time in hours.	Nitroso- amine.	Percentage yield of monomethylaniline
1	180°	3	4	14.5
2	180	6	11.5	21.0
3 <sup>1</sup>	200	13	28.0	51.0

<sup>1</sup> In Experiment 3 about 5 grams of a white solid separated on diluting the contents of the tube. This melted indefinitely at 144°, and after crystallisation from light petroleum indefinitely at about 160°. It was only superficially examined, and appeared to be a tertiary halogen-free base, possibly containing methyl groups in the benzene nucleus.

When 12 grams of dimethylaniline and 9.5 grams of aniline (molecular proportions) were heated for three hours at 220°, practically no monomethylaniline was produced.

Demethylation was found to occur when the two hydrochlorides were heated for three hours at 180°; thus, 13 grams of aniline hydrochloride and 15.8 grams of dimethylaniline hydrochloride (molecular proportions) gave 5.5 grams of the nitrosoamine, corresponding with a 20 per cent. yield of monomethylaniline.

#### *The Separation of Aniline and Monomethylaniline using Zinc Chloride.*

A mixture of aniline and monomethylaniline was treated with an aqueous solution of anhydrous zinc chloride. The precipitate was collected and thoroughly washed with light petroleum. After evaporation of the solvent, the residue of crude methylaniline was weighed and converted into the nitroso-derivative, which was removed from the mixture by extracting three times with ether, dried, and weighed.

The acid liquid which remained after the removal of the nitrosoamine, and contained traces of benzenediazonium chloride, was heated, saturated with salt, the phenol extracted with ether, and finally weighed. The aqueous filtrate from the zincchloride precipitate contained practically no aniline or methylaniline hydrochlorides.

\* In Experiment 1 half these quantities were employed.

The accuracy of this method was checked by regeneration of the aniline from a given weight of the zincichloride

*Analytical Results.*—*Taken:* Aniline 20 grams, methylaniline 20 grams, fused zinc chloride 22 grams, water 50 c.c.

*Obtained:* Zincichloride, 37 grams, whence aniline=19.2 grams. Phenylmethylnitrosoamine, 23.7 grams, whence methylaniline=18.7 grams. Phenol, 0.25 gram, whence aniline=0.25 gram.

There was also obtained 0.5 gram of bases from the aqueous filtrate from the zincichloride.

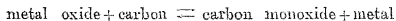
THE UNIVERSITY,  
BIRMINGHAM.

[Received, February 6th, 1919.]

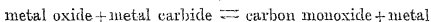
## XXIV.—*Equilibria in the Reduction of Oxides by Carbon.*

By ROLAND EDGAR SLADE and GEOFFREY ISHERWOOD HIGSON.

Equilibria of some reactions of the type:



or



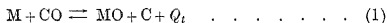
have been investigated.

In either of the above systems there are three components, namely, metal, carbon, and oxygen, and four phases, namely, metal, metal oxide, carbon (or carbide), and carbon monoxide (gas). The number of degrees of freedom is thus  $3 + 2 - 4 = 1$ . Therefore at one temperature there is one pressure of carbon monoxide which determines the equilibrium of the system.

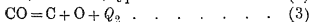
The following experimental method was adopted. A small quantity of the metal was heated in a vacuum to a certain temperature, and carbon monoxide was then admitted until the pressure was greater than the equilibrium pressure. The reaction proceeded in the direction from right to left, and carbon monoxide was absorbed until the equilibrium pressure was attained. Some carbon monoxide was then removed, when the reaction proceeded from left to right until the equilibrium pressure was again attained. If the carbon formed in the first part of the experiment did not remain as a separate phase either as a carbon or as a carbide, but formed a solid solution with the metal, there would be only two solid phases present with the gas phase; the system would there-

fore have two degrees of freedom, and the pressure of carbon monoxide would depend on the relative amounts of metal and carbon present, as well as on the temperature. When the equilibrium was attained from left to right, there was less carbon monoxide present than when the equilibrium was attained from right to left, therefore the equilibrium pressures would have been different in these two cases if there were only two solid phases present.

The equilibrium may be calculated from the heat of reaction by making use of the Nernst heat theorem. In the reaction



where M is the weight in grams of any metal combining with 16 grams of oxygen, and  $Q_t$  is the heat of reaction; in all cases  $Q_t$  is positive, so that increase in temperature will cause the formation of  $M + CO$ . That is to say,  $p_{co}$  increases with the temperature. This quantity of heat,  $Q_t$ , may be considered as the differences of two quantities of heat,  $Q_1$  and  $Q_2$ , for if we write



then, on addition,  $M + CO = MO + C + (Q_1 + Q_2)$ .  $Q_2$ , the heat of dissociation of carbon monoxide, is  $-29,000$  calories, therefore

$$Q_t = Q_1 - 29,000 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Neglecting terms containing  $T^2$ , the Nernst heat theorem requires that

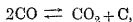
$$\log p_{co} = \frac{-Q_0}{4.571 T} + 1.75 \log T + 2.6 \quad . \quad . \quad . \quad (5)$$

where  $Q_0$  is the heat of reaction at absolute zero.

The thermodynamic constant used for carbon monoxide is the value given by Weigert in Abegg's "Handbuch." The relation between  $Q_0$  and  $Q_t$  is given by the equation

$$Q_0 = Q_t + 3.5T \quad . \quad . \quad . \quad . \quad . \quad (6)$$

*Limits of the Investigation.*—The equilibrium mentioned above could only be determined at temperatures at which the equilibrium,



is practically completely in the left-hand direction. Rhead and Wheeler (T., 1910, **97**, 2187; 1911, **99**, 1140) have investigated this equilibrium, and from their results it is possible to calculate the partial pressure of carbon dioxide in equilibrium with carbon monoxide at 760 mm. or 50 mm. These values are given in table I.



TABLE I.

Temperature.	Pressure of carbon dioxide in mm. when pressure of carbon monoxide is 760 mm.	Pressure of carbon dioxide in mm. when pressure of carbon monoxide is 50 mm.
850°	53.8	0.23
900	17.6	0.076
1000	4.6	0.0020
1100	0.90	0.00082
1200	0.46	0.00020

From these figures, it is seen that if the equilibrium pressure is as low as 50 mm., there is no complication due to the presence of carbon dioxide at temperatures from 850° upwards. If, however, the pressure is as great as 760 mm., the amount of carbon dioxide present is appreciable up to 1200°. If a carbide is present instead of free carbon, the ratio of carbon dioxide to carbon monoxide will be greater, for we have

$$\frac{p_{\text{CO}}^2}{p_{\text{CO}_2} p_c} = K,$$

and  $p_c$  (partial pressure of carbon vapour) will be lower over a carbide than over carbon.

In all our experiments, the equilibrium pressures were sufficiently low and the temperature was sufficiently high for the pressure of carbon dioxide to be negligible.

The metals with which we could determine the above equilibrium were only such as would fulfil the following conditions: (1) The metals must not be volatile at the temperature of the experiments. At these temperatures, the vapour pressure of the metal should certainly not be more than 0.25 mm., or it will distil rapidly on to parts of the platinum tube which are at a somewhat lower temperature, and probably attack the platinum. Platinum tubes were, in fact, destroyed by the volatility of boron and manganese. (2) The equilibrium pressure must not be greater than 50 mm. at 850°, or the quantity of carbon monoxide in the gas phase will be appreciable. (3) The equilibrium pressure must be sufficiently great to be measurable. It must be at least 1 mm. at 1300°. Applying the Nernst heat theorem to the equilibrium, we should only expect those elements of which the heat of oxidation, per gram-atom of oxygen, lies between 75,000 and 114,000 calories, to give an equilibrium pressure measurable in our apparatus. Of substances with known heats of oxidation, only silicon, boron, and manganese lie within this range. The only likely metals for which

the heats of oxidation were unknown, and which were readily obtainable, were vanadium, tantalum, and chromium.

*Apparatus.*—The furnace, which has been described by Slade (*Proc. Roy. Soc.*, 1912, [A], **87**, 519), consists of a platinum tube 2 cm. in diameter heated by a current of 300 to 400 amperes at 2 to 4 volts. The furnace is placed in a vessel which can be exhausted to prevent the platinum tube from collapsing under the pressure of the atmosphere. A silver capillary tube is used to connect the furnace with the glass tube leading to the pressure gauge. The temperatures were determined by means of a platinum-platinum (90 per cent.)–rhodium (10 per cent.) thermocouple. The couple was calibrated up to the melting point of copper, 1083°, and higher temperatures were determined by extrapolating by means of the formula

$$\log e = 1.22 \log t - 2.65,$$

where  $t$  is expressed in degrees centigrade and  $e$  in millivolts. The cold end of the couple was kept at 0°.

It was found to be impossible to use a platinum boat for any of the substances investigated, for although the temperatures were well below their melting points, they were rapidly alloyed with platinum. Accordingly, boats of unglazed Royal Berlin porcelain were employed.

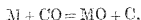
Pressures were read on a mercury vacuum manometer, behind which was a glass millimetre scale illuminated by a lamp and a milk-glass screen. The readings were made with a telescope, and were accurate to  $\pm 0.05$  mm.

The carbon monoxide was prepared by running pure formic acid into concentrated sulphuric acid at 70–80°. The gas, which was first passed through a long tube of soda-lime and then through a similar tube of phosphoric oxide, was collected and stored over mercury in a vessel of 1 litre capacity.

The gas was led from the reservoir to the furnace and pressure gauge by means of a tube, in which were placed two taps separated by a capillary tube of such dimensions that the volume between the two taps was 0.2 c.c. By filling this tube with carbon monoxide at the ordinary temperature, then closing one tap and opening the other, 0.2 c.c. of carbon monoxide was allowed to flow into the exhausted furnace and the tubes connecting the furnace to the gauge and pump. The total volume of this part of the apparatus was about 50 c.c., and when the furnace was heated to about 1200°, its effective volume was about 30 c.c., so that the introduction of 0.2 c.c. under a pressure of one atmosphere caused a rise of pressure of  $\frac{0.2}{30}$  atmosphere, or about 5 mm. of mercury.

In most of the experiments, 0.1 gram of the metal under investigation was introduced into the boat. That this was sufficient may be seen from the following considerations.

If the reaction is



where M is two equivalents of an element, then two gram-equivalents of the element would react with 22,400 c.c. of carbon monoxide. If the pressure in the furnace was 60 mm., which was the maximum pressure used in several cases, the volume of gas contained in the furnace was 2.4 c.c. when measured at N.T.P., therefore to absorb all this gas,  $\frac{2.4}{22,400} \times 2 = 2.2 \times 10^{-4}$  gram-equivalent

of the element would be required. If the equivalent were as great as 100, only 0.02 gram would be required. The metal was usually broken into small pieces, as the velocity of the action must be proportional to the surface exposed.

*Experiments with Vanadium.*—As vanadium is a very refractory substance and is difficultly reducible (that is, the oxide has a high heat of formation), it was decided to attempt to measure the reduction equilibrium.

Some preliminary experiments were made on the action of vanadium on platinum and the melting point of vanadium. The vanadium was placed, in very small pieces (about 0.5 mm. in diameter and less), on a platinum strip which was heated in an atmosphere of hydrogen by an electric current. At 1400°, the vanadium adhered to the strip when the heating had been carried on for some three minutes. The temperature was determined by means of a Wanner pyrometer, correction being made for black-body radiation of the platinum. In another experiment, the strip was dusted with powdered vanadium and heated rapidly until it fused at one point. Examination under the microscope showed that the vanadium had then fused into globules just round the portion of the strip which had fused. The melting point of this vanadium is therefore just below the melting point of platinum, namely, 1760°. The vanadium had been prepared in the electric furnace, and contained 4.6 per cent. of carbon. The carbon probably exists as the carbide, VC, and may be present in solid solution, although the fact that so much carbon is present makes it seem probable that the carbide exists as a separate phase.

*Experiments.*—0.0636 Gram of the metal was placed in an unglazed porcelain boat in the platinum tube furnace. The furnace was exhausted and left for sixteen hours, when no rise of pressure was noticeable. The temperature was raised to 1000°, and the occluded gas from the boat pumped off; 0.2 c.c. of carbon mon-

oxide was then admitted, and this raised the pressure to 6 mm., at which it remained. Therefore the equilibrium pressure was greater than this, or the velocity of reaction at this temperature was very small. The latter was found to be the case, for when the pressure of carbon monoxide had been increased to 60 mm., there was still no reaction. The temperature was then raised to 1340°, and maintained at this temperature for four and a-half hours. During this time, the pressure fell at first rapidly, and finally became steady at 1.7 mm. The temperature was then reduced to 1145°, where it was maintained for thirty minutes. The pressure fell rapidly to 0.55 mm., where it remained constant. The temperature was then lowered to 900°, when the pressure fell only to 0.2 mm.

On the following day, the furnace was heated to 1340° and the temperature kept constant. In one hour the pressure rose to 1.2 mm., at which it remained constant for three and a-half hours.

The equilibrium pressure at 1340° was therefore between 1.7 and 1.2 mm. The mean of these values is 1.45 mm. At lower temperatures, the equilibrium was attained too slowly to be determined.

The reaction is probably



The value

$$p_{\text{CO}} = \frac{1.45}{760} \text{ atm. at } 1340^\circ$$

gives, by the Nernst heat theorem, the value

$$Q_0 = 80,875 \text{ cal.}$$

Substituting this in equation (5), we find that

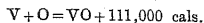
$$p_{\text{CO}} = 1 \text{ atmosphere at } 1827^\circ.$$

This is the temperature at which vanadium oxide would be reduced by the carbide under a pressure of one atmosphere.

There is no direct evidence as to the heat of formation of vanadium carbide, that is, of the reaction



but usually the heats of formation of carbides are small (Wartenberg, *Zeitsch. anorg. Chem.*, 1907, 52, 299), that is to say, not greater than 2000—3000 calories per gram-atom of carbon. If this heat of formation of the carbide is neglected, an approximate value of the heat of oxidation of vanadium at 20° can be obtained:



Not much trust can be placed in this value, however, for the carbide may be in solid solution in the metal and not as a separate phase.

*Experiments with Tantalum.*—The tantalum used was a portion of a specimen obtained from the late Dr. Werner von Bolton, and used by von Hevesy and Slade to determine the electrode potential of tantalum. It was in the form of a rolled sheet about 0.25 mm. thick. As only a small quantity of the metal was available, 0.035 gram was used in each experiment. If the tantalum was oxidised to the oxide,  $Ta_2O_5$ , this metal would absorb 3.5 c.c. of carbon monoxide. In the first experiment with tantalum, the metal was in the form of one piece of sheet. At  $1000^\circ$ , 2 c.c. of carbon monoxide were admitted ( $p=60$  mm.); the pressure fell, and in two hours became constant at 0.7 mm. The temperature was then raised to  $1200^\circ$  and 0.6 c.c. of carbon monoxide was admitted, so that the pressure was raised to 14 mm. As the pressure did not fall, more carbon monoxide was admitted until the pressure was 40 mm., but there was still no action. The furnace was therefore exhausted, but no appreciable rise in pressure took place in two hours. It therefore seemed probable that the constant pressure of 0.7 mm. obtained at  $1000^\circ$  was not a true equilibrium pressure, but that the equilibrium pressure, even at  $1200^\circ$ , was very low indeed.

In the next experiment the same quantity of metal was used, but it was cut into as many strips as possible, in order to increase the surface. After pumping out all gases from the boat at  $1150^\circ$ , 0.4 c.c. of carbon monoxide was admitted, so as to raise the pressure to about 13 mm. In half an hour the pressure fell to 0.2 mm., and then became constant, and remained so for half an hour. An attempt was now made to reach the equilibrium from the low pressure side. The furnace was exhausted and the temperature was raised to  $1270^\circ$ . In four hours the pressure rose slightly above 0.1 mm. (perhaps 0.12 mm.), and remained constant for about three hours. Carbon monoxide (about 0.1 c.c.) was then admitted to raise the pressure to 2.5 mm., and in one hour the pressure fell to 0.1 mm. This value is therefore the equilibrium pressure at  $1270^\circ$ .

It was impossible to determine the equilibrium at a higher temperature, because at this stage of the work the platinum tube had become weakened and slowly collapsed when kept exhausted for several hours at  $1270^\circ$ , although the external pressure on the tube was only 30–40 mm. of mercury.

*Experiments with Chromium.*—The temperature of reduction of chromium sesquioxide was determined by Greenwood (T., 1908, 93, 1438), who found that this oxide was reduced at  $1195^\circ$  under a

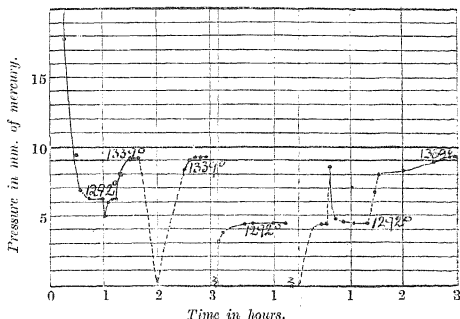
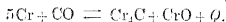
pressure of 2 mm. The boiling point of chromium is  $3200^{\circ}$  (Greenwood), and from this value the vapour pressure of liquid chromium can be calculated to be 0.07 mm. at  $1000^{\circ}$ , 0.078 mm. at  $1100^{\circ}$ , 0.7 mm. at  $1200^{\circ}$ , and 1.12 mm. at  $1300^{\circ}$ . It was therefore not safe to heat chromium to a much higher temperature than  $1200^{\circ}$  in the platinum furnace.

The chromium had been prepared by the Goldschmidt method, and therefore contained a trace of aluminium. As aluminium is easily and completely oxidised by carbon monoxide, it is probable that it would only have a very slight influence on the equilibrium.

0.45 Gram of metal, in the form of a coarse powder, was used in the first experiment. The furnace was heated to  $936^{\circ}$ , and all adsorbed gases were pumped out. Carbon monoxide was then admitted until the pressure was 100 mm. In nine and a-half hours the pressure fell to 22 mm., but did not appear to be approaching a steady value. After remaining for eighty-five hours, the furnace was heated to  $1010^{\circ}$  and carbon monoxide admitted until the pressure was 50 mm. In six hours the pressure fell to 0.75 mm., and appeared to be constant. After eighteen hours, the temperature was raised to  $1292^{\circ}$ , and carbon monoxide admitted until the pressure was 63 mm. In forty-five minutes the pressure fell to 6.2 mm., and remained constant. Carbon monoxide was then pumped out until the pressure fell to 5 mm. In fifteen minutes the pressure rose to 6.2 mm., and remained constant. The temperature was then raised to  $1339^{\circ}$ , and in twenty-five minutes the pressure had risen to 9.1 mm., and become constant. The furnace was then cooled, and next day was heated to  $1339^{\circ}$ . In twenty minutes the pressure rose to 9.2 mm. The furnace was now cooled to  $1292^{\circ}$ , and carbon monoxide was pumped off until the pressure was less than 1 mm. In an hour the pressure became constant at 4.4 mm. The furnace was cooled, and the next day was heated to  $1292^{\circ}$ ; the pressure rose to 4.4 mm. Carbon monoxide was then admitted until the pressure was 8.6 mm. In forty-five minutes the pressure fell to 4.4 mm. The temperature was now raised to  $1339^{\circ}$ , when the pressure rose to 9.2 mm. In the figure are given some of the time-pressure curves obtained. These show how accurately the results could be reproduced.

A new sample of chromium (0.45 gram) was now introduced into the furnace, and the temperature was raised to  $1292^{\circ}$ , carbon monoxide being admitted until the pressure was 15 mm. In twenty minutes the pressure fell to 6.2 mm., and remained constant at this value for one hour. The temperature was then raised to  $1339^{\circ}$ , and the pressure rose to 9.1 mm., but the platinum tube began to leak, owing to its being attacked by the chromium, which had distilled on to it during this and former experiments.

Table II shows the values for the equilibrium pressure obtained with chromium. All these equilibrium pressures were obtained twice from each side. The high value at  $1292^\circ$  is the value obtained when the furnace had not been raised to a higher temperature. After the temperature had been raised to  $1339^\circ$  and lowered again to  $1292^\circ$ , the equilibrium pressure was 4.4 mm., and this value could be obtained again and again. Since chromium easily forms a carbide, it is probable that the reaction taking place was



Calculating the heat of reaction per gram-atom of oxygen at  $1315^\circ$  from the Nernst formula and the van't Hoff formula, the values given in table II are obtained.

TABLE II.

Temperature.	Pressure of carbon monoxide in mm.	$Q_t$ calculated, Nernst.	$Q_t$ calculated, van't Hoff.
$1292^\circ$	6.2	73,600	—
1339	9.2	69,200	77,000
1292	4.4	69,200	

The value 77,000 calories is the heat of reaction calculated from the integrated form of the van't Hoff equation,

$$Q_t = -4571 (\log p_2 - \log p_1) \frac{T_1 T_2}{T_2 - T_1}.$$

In this method of calculating  $Q_t$ , an error of 0.1 mm. in the determination of the equilibrium at  $1292^\circ$  would make a difference of a little more than 1000 calories in the value of  $Q_t$ . The assumption on which this formula is based, however, is only that the heat

of reaction does not change appreciably between the two temperatures. That two different values were obtained for the equilibrium at 1292°, according to whether the furnace had been heated up to 1339° or not, must be explained by supposing that the substances in equilibrium were different in the two cases. It is very improbable that the first value is due to the presence of a trace of aluminium in the metal, for the presence of aluminium would be expected to lower rather than to raise the equilibrium pressure, and in the two experiments in which the pressure was 6.2 mm., very different amounts of carbon monoxide had been absorbed by the same amount of metal. In the first experiment, 6—7 c.c. of carbon monoxide, and in the second case only 0.6 c.c., were absorbed.

The equilibrium in the gas phase is represented by

$$p_{\text{CO}} = K \cdot \frac{p_{\text{carbide}}}{p_{\text{metal}}} \cdot \frac{p_{\text{oxide}}}{p_{\text{metal}}}$$

The change in the system caused by raising the temperature to 1339° was to give a lower equilibrium pressure at 1292°, and this must be due to (1) increase in the partial pressure of chromium, (2) lowering of the partial pressure of the carbide, or (3) lowering of the partial pressure of the oxide.

Case (1) might be caused by the existence of a transition point of chromium between 1292° and 1339°. At first, the metal is in the  $\alpha$ -form, stable at lower temperatures; on heating, the metal would change to the other, or  $\beta$ -form, and on cooling to 1292° would not revert to the  $\alpha$ -form, but remain in the unstable  $\beta$ -form, which would have a higher vapour pressure than the  $\alpha$ -form.

Case (2) might be caused by the formation of an unstable carbide in the first instance, which on heating to 1339° changes into the stable form. On cooling now to the lower temperature, the unstable carbide is not formed in the presence of the more stable one.

Case (3) might be caused by the chromium oxide combining with the silica in the boat to form a silicate, but this reaction should not be different after the furnace had been raised to the higher temperature. The first explanation seems the more probable.

This investigation was carried out in the Muspratt Laboratory of Physical Chemistry, University of Liverpool.

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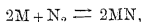
[Received, February 14th, 1919.]



XXV.—*The Dissociation Pressures of some Nitrides.*

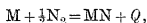
By ROLAND EDGAR SLADE and GEOFFREY ISHERWOOD HIGSON.

Equilibria of the type



where  $M$  is three equivalents of a metal, have been investigated. In this system there are two components, namely, metal and nitrogen, and three phases, namely, metal, nitride, and nitrogen. The number of degrees of freedom is thus  $2 + 2 - 3 = 1$ , and therefore at one temperature there is one pressure of the nitrogen which determines the equilibrium of the dissociation. If the nitride dissolves in the metal as a solid solution, there are only two phases, and the number of the degrees of freedom is therefore two. The equilibrium will then be determined, not only by the pressure of the nitrogen, but also by the composition of the solid phase.

Applying the Nernst heat theorem to the equilibrium



where  $Q$  is the heat evolved when half a gram-molecule of nitrogen combines with the metal, we have

$$\log p_{N_2} = -\frac{Q_0}{4.571T} + 1.75 \log T + 2.6$$

and

$$Q_t = Q_0 - 3.5T,$$

where  $Q_0$  and  $Q_t$ , respectively, are the heats of reaction at absolute zero and some other temperature,  $T$ . As the heats of formation of the nitrides investigated were unknown, it is impossible to apply these equations to determine the value of  $p_{N_2}$ , but it will be seen that the pressure of nitrogen at  $1127^\circ$  would be 1 mm. if the heat of formation of the nitride were 70,600 cal. and 60 mm. if the heat of formation were 59,000 cal.

## EXPERIMENTAL.

The furnace used for the determination of the equilibria is described in the preceding paper.

Nitrogen was prepared by heating a solution containing ammonium chloride, potassium nitrate, and potassium dichromate. The dichromate served to oxidise any oxides of nitrogen to nitric acid, which was absorbed by passing the gas through a long tube of soda-lime. The nitrogen was then dried by passage through a long tube of phosphoric oxide.

The equilibria were determined by heating small quantities of

the metal to a known temperature, introducing nitrogen into the furnace, and determining the value to which the pressure fell. Nitrogen was then pumped out, and the equilibrium was determined from the low-pressure side.

*Vanadium*.—This metal is known to form two nitrides, VN and VN<sub>2</sub>.

At 1203°, the equilibrium pressure was found to be slightly less than 0.2 mm., and at 1271° slightly less than 1.5 mm. The equilibrium pressure is somewhere near these values, but equilibrium was attained very slowly, and it was impossible to heat the platinum tube in use at that time to a higher temperature.

*Boron*.—An attempt was made to determine the dissociation pressure of boron nitride at 1100° and 1240°.

At 1100°, the velocity was too low for the equilibrium to be determined. At 1240°, the pressure of nitrogen fell from 26.4 mm. to 9.4 mm. in six hours, and appeared to be approaching the constant value of about 9 mm., but the boron attacked the platinum tube and caused it to leak, so that further experiments could not be made.

*Tantalum*.—Tantalum is known to form two stable nitrides, TaN and Ta<sub>3</sub>N<sub>5</sub>. In our experiments, it is probable that the lower nitride, TaN, was formed.

When the metal was heated at 1170° in nitrogen under 15 mm. pressure, the gas was slowly absorbed until the pressure fell to 0.5 mm. The furnace was then exhausted to 0.05 mm. The pressure rose in two hours to 0.4 mm.

In another experiment, at 1308°, the pressure fell from 9 mm. to 1.2 mm. in one and a-half hours, and remained constant for half an hour. The furnace was then allowed to cool. Next day it was completely exhausted, and again heated to 1308°. The pressure rose to 0.8 mm., and remained constant at this value for two hours.

#### Summary of Results.

	Temperature.	Pressure of nitrogen.	Heat of formation of nitride, that is, $Q_p$ , calculated from Nernst's formula.
Vanadium	1203°	Not greater than 0.2 mm.	79,200 cals.
	1271	" " 1.5 "	77,200 "
Boron ...	1222	" " 9.4 "	About 69,000 "
Tantalum	1170	0.4—0.5 mm.	74,700—75,500 cals.
	1308	0.8—1.2 "	79,900—82,800 "

This investigation was carried out in the Muspratt Laboratory of Physical Chemistry, University of Liverpool.

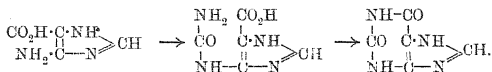
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[Received, February 14th, 1919.]

XXVI.—*Nitro-, Arylazo-, and Amino-glyoxalines.*

By ROBERT GEORGE FARGHER and FRANK LEE PYMAN.

THIS investigation was begun with the object of effecting the synthesis of purine derivatives by a method complementary to those which have been employed hitherto. In these, the pyrimidine nucleus is first built up and the glyoxaline ring closed subsequently. We proposed to prepare 4-aminoglyoxaline-5-carboxylic acid,\* condense it with cyanic acid, and eliminate water with the production of xanthine.



Such a synthesis would be of interest in view of the suggestion that purine derivatives originate from histidine in the animal body (compare Hopkins, T., 1916, 109, 629).

Although the starting material for the proposed synthesis, 4-aminoglyoxaline-5-carboxylic acid, was unknown, we did not anticipate that its preparation would offer any serious difficulty. We have, however, so far failed to obtain this substance, and now give an account of our attempts to prepare this and other amino-substituted glyoxalines.

An account of the investigation may be subdivided under three headings: first, the preparation of the glyoxalines and their carboxylic acids, which were required as starting materials; second, the preparation and properties of nitroglyoxalines; and last, the preparation and properties of arylazoglyoxalines.

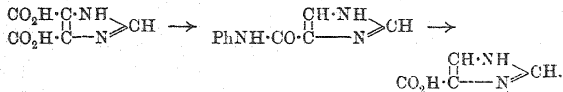
(1) *The Preparation of Glyoxalines and their Carboxylic Acids.*—For the purpose of this investigation, it was necessary to prepare considerable quantities of glyoxaline-4:5-dicarboxylic acid, the most convenient source of glyoxaline. This acid was first prepared by Maquenne (*Ann. chim. phys.*, 1891, [vi], 24, 525), by mixing aqueous solutions of nitrotartaric acid and hexamethylenetetramine, adding ammonia, and allowing the mixture to become hot, and subsequently by Dedichen (*Ber.*, 1906, 39, 1835), who replaced the hexamethylenetetramine by formaldehyde. We have carried out a large number of experiments on the best conditions for the pre-

\* In glyoxalines containing a free imino-group, the 4- and 5-positions are equivalent.

paration of this acid, and find that to obtain a good yield it is essential that the reaction mixture should be kept cold.

A number of experiments were carried out with the object of effecting the partial decarboxylation of glyoxaline-4:5-dicarboxylic acid, and thus producing glyoxaline-4-carboxylic acid by a more convenient and economical process than that previously employed, where six operations are required in its synthesis from citric acid through 4-hydroxymethylglyoxaline (T., 1911, **99**, 668; 1916, **109**, 186). When the acid is heated with water, 10 per cent. hydrochloric acid, or concentrated hydrochloric acid, little decarboxylation takes place below 180°, but above this temperature, the action proceeds more readily, glyoxaline being the main product, whilst a small proportion of glyoxaline-4-carboxylic acid can be isolated provided that the heating has not been too prolonged. When the acid is heated with an excess of concentrated ammonia at 180° to 200°, the main product is glyoxaline,\* and a similar result is obtained by heating the aqueous solution of the mono-sodium salt.

The desired result can be obtained, however, by boiling the acid with aniline, when the *anilide* of glyoxaline-4-carboxylic acid is formed in a yield amounting to 45 per cent. of the theoretical. From this, the acid is readily prepared by hydrolysis.



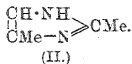
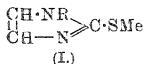
For the purpose of orientation, it was necessary to prepare glyoxalines substituted in the 2-, 4:5-, and 2:4:5-positions. The 2-alkylglyoxalines were prepared by suitable modifications of Maquenne's methods. From 2-methylglyoxaline-4:5-dicarboxylic acid, 2-methylglyoxaline-4-carboxylic acid was obtained through its *anilide*.

As representatives of 4:5- and 2:4:5-substituted glyoxalines, 4:5-dimethylglyoxaline and 2:4:5-trimethylglyoxaline were prepared by modification of known methods.

(2) *Nitroglyoxalines*.—The nitration of various glyoxalines has led to the formation of mononitroglyoxalines in the hands of several observers. In some cases the nitro-group evidently enters the 4-(or 5-)position, since no other position is vacant; for instance, in the nitration of 2-methylthiol-1-phenyl (and 1-methyl)glyoxaline

\* We were unable to find any evidence of the formation of the imide of glyoxaline-4:5-dicarboxylic acid, from which the desired 5-aminoglyoxaline-4-carboxylic acid might have been obtained by the action of hypobromous acid.

(I) (Wohl and Marckwald, *Ber.*, 1888, **22**, 568, 1353) and 2:4-dimethylglyoxaline (II) (Windaus, *Ber.*, 1909, **42**, 758):



The orientation of the nitro-group in nitroglyoxaline itself (Rung and M. Behrend, *Annalen*, 1892, **271**, 28; R. Behrend and Schmitz, *ibid.*, 1893, **277**, 338) and in nitro-4-methylglyoxaline has not been determined previously, but an indication that the latter contains the nitro-group in the 5-position is afforded by Windaus's observation (*loc. cit.*) of its close similarity to 5-nitro-2:4-dimethylglyoxaline.

Moreover, whilst 4-nitro-2-methylglyoxaline is readily prepared, we were unable to obtain a nitro-derivative of 4:5-dimethylglyoxaline, for in this case part of the base was completely oxidised, whilst a considerable proportion remained unchanged, and the only isolable derivative was the nitrate of 4-methylglyoxaline-5-carboxylic acid, which has been described by Gerngross (*Ber.*, 1912, **45**, 509).

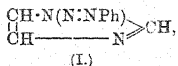
The inability of a glyoxaline substituted in both the 4- and 5-positions to form a nitro-derivative indicates that the nitroglyoxalines contain the substituent in the 4-(or 5-)position. This view is confirmed by their behaviour on reduction. Wohl and Marckwald (*loc. cit.*) attempted to reduce the 4-(or 5-)nitro-2-methylthiol-1-phenyl-(and 1-methyl)glyoxalines to the corresponding amines, but obtained only decomposition products, including methyl mercaptan. Similarly, we find that 4-nitro-2-methylglyoxaline undergoes fission on reduction with tin and hydrochloric acid, two of the three atoms of nitrogen in the molecule appearing in the form of ammonia.\* Since precisely the same result is obtained with nitroglyoxaline and nitro-4-methylglyoxaline, whilst it is shown below that 2-aminoglyoxalines are stable, it is clear that these nitro-derivatives are 4-nitroglyoxaline and 5-nitro-4-methylglyoxaline respectively.

Before we had arrived at this conclusion, we were anxious to prepare some of the nitroglyoxaline-4-carboxylic acid, which Windaus and Opitz (*Ber.*, 1911, **44**, 1721) obtained by the action of boiling 25 per cent. nitric acid on 4-β-hydroxyethylglyoxaline.

\* The first stage in the disintegration of the 4-aminoglyoxalines is probably the elimination of the amino-group as ammonia, with the formation of a glyoxalone, for certain members of the purine group—also derivatives of 4-aminoglyoxaline—have been shown to undergo hydrolysis in this manner (compare, for instance, Tafel and Mayer, *Ber.*, 1908, **41**, 2546; Biltz, *Ber.*, 1910, **43**, 1589).

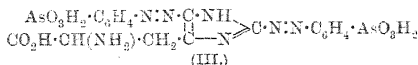
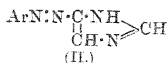
These authors state that the yield of 4- $\beta$ -hydroxyethylglyoxaline, obtained by the action of barium nitrite on 4- $\beta$ -aminoethylglyoxaline hydrochloride, was so poor that the nitro-compound was not available in sufficient quantity for further study. It appeared to us, however, that this nitro-compound might be obtained by the action of nitric acid on other more readily accessible derivatives of glyoxaline containing a side-chain of carbon atoms in the 4-position, and in the first place we employed compounds containing two carbon atoms in the side-chains, like Windaus's starting material. The results were disappointing; 4- $\beta$ -aminoethylglyoxaline, when boiled with 50 per cent. nitric acid for nine hours, was mainly recovered unchanged, whilst 4-cyanomethylglyoxaline was converted under the same conditions almost quantitatively into glyoxaline-4-acetic acid. Attempts to nitrate glyoxaline-4-carboxylic acid and glyoxaline-4:5-dicarboxylic acid were likewise unsuccessful. The prospect of nitrating 4-hydroxymethylglyoxaline was not hopeful, for it has been shown previously (T., 1916, 109, 186) that hot concentrated nitric acid converts it into glyoxaline-4-formaldehyde and glyoxaline-4-carboxylic acid. It has now been found that the alcohol gives the same products when digested on the water-bath with fuming nitric acid, whilst it can be recovered almost quantitatively after boiling with ten parts of 25 per cent. nitric acid for four hours. On the other hand, the nitration of 4-hydroxymethylglyoxaline with nitric and sulphuric acids gave rise to a product which was not obtained in crystalline form, but further study of this was omitted in view of the peculiar behaviour of the simple nitroglyoxalines on reduction.

(3) *Arylazoglyoxalines*.—The constitution of the arylazo-derivatives of simple glyoxalines has not been settled hitherto. Rung and Behrend (*Annalen*, 1892, 271, 28), who first isolated benzene-azoglyoxaline, considered it to be a diazoimino-compound (I), because boiling acids decomposed it with the formation of nitrogen



and glyoxaline. Burian (*Ber.*, 1904, 37, 696), who prepared many arylazoglyoxalines from diazobenzene-*p*-sulphonic acid and various glyoxalines, adopted the same view of the constitution of these compounds on other grounds, namely, because all the glyoxalines substituted in some or all of the 2-, 4-, and 5-positions which he examined coupled with the diazonium salt, whilst 1-substituted glyoxalines did not. Pauly (*Zeitsch. physiol. Chem.*, 1904, 42, 508), however, pointed out the possibility that the arylazo-

glyoxalines were true *C*-azo-compounds (II) similar to those obtained from pyrrole, and later (*ibid.*, 1915, 94, 284) attributed the probable formula (III) given below to the compound obtained by the action of diazotised arsanilic acid on histidine, owing to its stability towards acids. Whilst in the case of these simple

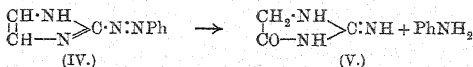


glyoxalines the orientation of the arylazo-group is uncertain, the constitution of the arylazopurines is known, for Hans Fischer (*Zeitsch. physiol. Chem.*, 1909, 60, 69) has shown that the arylazo-group enters the 8-position of the purine nucleus—the 2-position of its glyoxaline ring—by reducing arylazopurines to 8-aminopurines.

In view of this result, it appeared to us probable that the arylazo-derivatives of simple glyoxalines were also *C*-azo-compounds, as Pauly suggested, and it was of interest to determine whether the arylazo-group entered the 2- or the 4-position, and the nature of the products obtained on reduction.

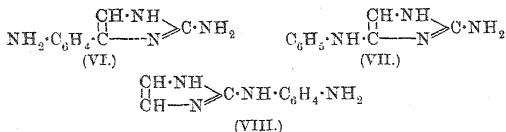
The benzeneazoglyoxaline of Rung and Behrend was first examined. By the method of these workers, it is obtained in poor yield, but by the action of benzenediazonium chloride on one molecular proportion of glyoxaline in an excess of aqueous sodium carbonate, it is readily obtained mixed with a little 2:4:5-*tris*-benzeneazoglyoxaline. 2-Benzeneazoglyoxaline melts at 190° (corr.), and it is therefore evident that the specimen prepared by Rung and Behrend, melting at 177–178°, was impure. The pure substance is reasonably stable towards boiling 10 per cent. hydrochloric acid, for a considerable proportion can be recovered unchanged after two hours.

The constitution of 2-benzeneazoglyoxaline (IV) was proved by reduction. With zinc dust and hot acetic acid, it yields aniline and glycocyanidine\* (V), the formation of the latter showing that the benzeneazo-group is attached to the 2-position of the ring.

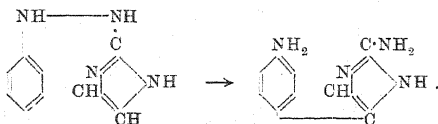


\* The conversion of glyoxaline into glycocyanidine and 2-aminoglyoxaline, both derivatives of guanidine, is of biochemical interest, firstly, because creatinine is the *N*-methyl derivative of glycocyanidine, and secondly, on account of the similar behaviour of histidine and arginine in purine metabolism (compare Hopkins, *loc. cit.*).

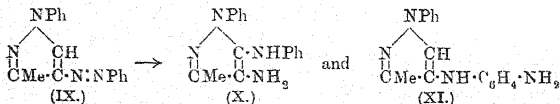
This result is confirmed by the formation of a small amount of guanidine on the reduction of 2-benzeneazoglyoxaline with stannous chloride. In this reduction, a small quantity of 2-aminoglyoxaline is formed and some aniline, but the main product is 2-amino-4-*p*-aminophenylglyoxaline (VI), a compound resulting from a change of the benzidine type. It is also formed in small proportion in the reduction with zinc dust and acetic acid.



Its constitution was proved by the oxidation of its diacetyl derivative with potassium permanganate, when *p*-acetylaminobenzoic acid was formed. This result eliminated the possibility that the compound had one of the two formulæ (VII) or (VIII), representing substances formed by a change of the semidine type. The occurrence of a rearrangement of the benzidine type in a five-membered heterocyclic nucleus seems remarkable at first sight, but a closer inspection of the formula shows that the conjugated system connecting the 2- and 5-carbon atoms of the glyoxaline ring is similar to that existing in the benzene nucleus.



Whilst no other case of the benzidine type of change in a heterocyclic nucleus has been observed previously, so far as we are aware, Michaelis and Schäfer (*Annalen*, 1915, **407**, 229) have obtained by the reduction of 1-phenyl-3-methyl-4-benzeneazopyrazole (IX) the two isomerides (X) and (XI) which result from the two possible changes of the semidine type.



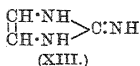
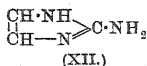
Owing to the formation of 2-amino-4-*p*-aminophenylglyoxaline in the reduction of 2-benzeneazoglyoxaline, the yield of 2-amino-



glyoxaline is small, so for the preparation of this substance the reduction of an arylazoglyoxaline containing a substituent in the para-position of the benzene nucleus was undertaken.

2-*p*-Bromobenzeneazoglyoxaline is the main product of the interaction of *p*-bromobenzenediazonium chloride and glyoxaline in aqueous sodium carbonate, only a very small proportion of 4-*p*-bromobenzeneazoglyoxaline being formed. The reduction of 2-*p*-bromobenzeneazoglyoxaline with stannous chloride gave 2-aminoglyoxaline in a yield of 56 per cent. of the theoretical, together with aniline, guanidine, some 2-amino-4-*p*-aminophenylglyoxaline, and a small quantity of a base,  $C_9H_9N_4Br$ , which is probably 2-5'-bromo-2'-aminoanilinoxyoxaline (compare p. 246).

2-Aminoglyoxaline is a monacidic base yielding crystalline salts, but the free base has not been obtained in a crystalline form.



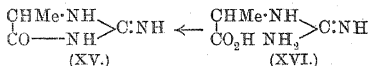
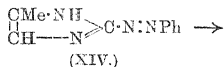
For this compound, the tautomeric formulæ (XII) and (XIII) are possible. The first is supported by the production of a red colour when the substance is mixed with sodium diazobenzene-*p*-sulphonate, and by the fact that, after treatment with nitrous acid, it couples with phenols. An indication that it can also react according to the formula (XIII)—which represents an unsaturated compound no longer containing the glyoxaline ring—is given by its behaviour towards permanganate, for 2-aminoglyoxaline and all the substituted 2-aminoglyoxalines described in this paper reduce cold aqueous acid potassium permanganate, and in this respect resemble the 2-thioglyoxalines (compare T., 1911, 99, 2173), whereas glyoxaline and its homologues are stable to this reagent, although they reduce alkaline permanganate, giving green solutions.

2-Aminoglyoxaline yields a *monoacetyl* and a *monobenzoyl* derivative, which are stable to cold aqueous acid permanganate.

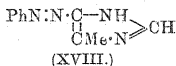
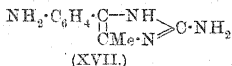
2-Aminoglyoxaline does not combine with benzaldehyde in acetic acid solution. Moreover, 2-amino-5-*p*-aminophenyl-4-methylglyoxaline (XVII) yields only a monobenzylidene compound under these conditions, doubtless 2-amino-5-*p*-benzylideneaminophenyl-4-methylglyoxaline. This behaviour, therefore, serves to differentiate between 2-aminoglyoxalines and homologues of aniline, and is employed later in the determination of constitution.

The action of benzenediazonium chloride on 4-methylglyoxaline proceeded quite differently from its action on glyoxaline. Instead of the 2-substituted arylazo-compound being formed predominantly,

nearly equal quantities of 2-benzeneazo-4-methylglyoxaline, 5-benzeneazo-4-methylglyoxaline, and 2:5-bisbenzeneazo-4-methylglyoxaline were obtained. The constitution of 2-benzeneazo-4-methylglyoxaline (XIV) follows from the fact that it yields, on reduction with zinc dust and acetic acid, alacreatinine (XV), a compound previously synthesised by Baumann (*Annalen*, 1873, 167, 83) by the elimination of water from  $\alpha$ -guanidinopropionic acid (XVI).



This change is precisely similar to the formation of glyco-cyamidine from 2-benzeneazoglyoxaline. 2-Benzeneazo-4-methylglyoxaline behaves in the same way as 2-benzeneazoglyoxaline on reduction with stannous chloride, the principal product of the reaction being 2-amino-5-p-aminophenyl-4-methylglyoxaline (XVII), a compound having similar properties to 2-amino-4-p-aminophenyglyoxaline.



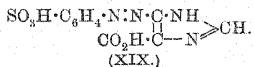
The constitution of 5-benzeneazo-4-methylglyoxaline (XVIII) could not be proved directly as in the case of the 2-isomeride. On reduction, aniline and a considerable amount of ammonia were formed, together with other products, which included a base,  $\text{C}_6\text{H}_{10}\text{ON}_2$  (p. 254), when stannous chloride was employed as the reducing agent, and a base,  $\text{C}_{10}\text{H}_{11}\text{ON}_3$  (p. 255), when zinc dust and acetic acid were used. The disintegration of the molecule indicated by the formation of ammonia is similar to that occurring in the reduction of the 4-nitroglyoxalines, and affords evidence that the constitution of the compound is represented correctly by the formula of 5-benzeneazo-4-methylglyoxaline. The formula is supported by the fact that the compound is soluble in dilute aqueous sodium hydroxide, which indicates that the imino-group is unsubstituted. Moreover, it is fairly stable towards boiling dilute acids. Its properties are not therefore in accord with those of a compound represented by the alternative formula, 1-benzeneazo-4-methylglyoxaline.

That aryldiazonium salts are capable of substituting the 4-position of the glyoxaline ring follows from the reduction of 2-phenyl-

4-p-bromobenzeneazoglyoxaline,  $C_{15}H_{11}N_4Br$ , for a compound,  $C_{15}H_{13}N_4Br$ , is produced, which is evidently derived from the corresponding hydrazo-compound by a change of the semidine or benzidine type (compare p. 257).

The polyarylazoglyoxalines—2:4:5-trisbenzeneazoglyoxaline and 2:5-bisbenzeneazo-4-methylglyoxaline—are insoluble in dilute mineral acids, and are decomposed on boiling with 10 per cent. hydrochloric acid. Nevertheless, we regard them as *O*-azo-compounds, because they are soluble to some extent in aqueous sodium hydroxide. In the case of the second compound, we have established the fact that it is precipitated unchanged from its solution in aqueous sodium hydroxide by means of acetic acid. The fact that the number of arylazo-groups in the polyarylazo-compounds corresponds with the number of nuclear methine groups in the parent glyoxaline points in the same direction.

The interaction of glyoxaline-4:5-dicarboxylic acid and diazobenzene-*p*-sulphonic acid was studied by Burian (*loc. cit.*), who found, that carbon dioxide was liberated, and described a product forming yellow needles or red, microscopic prisms which gave on analysis results indicating that it was a compound derived from one molecular proportion of diazobenzene-*p*-sulphonic acid and one of glyoxaline-4-carboxylic acid,  $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_3\text{H}_2\text{N}_2\cdot\text{CO}_2\text{H}$ . Burian regarded this as a 1-substituted arylazoglyoxaline, but we thought it more probable that the arylazo-group had displaced a carboxyl group in the 4-(or 5)-position, and that the compound was 5-*p*-sulphobenzeneazoglyoxaline-4-carboxylic acid (XIX).



This compound would yield 5-aminoglyoxaline-4-carboxylic acid if a suitable method of reduction could be found, and we therefore attempted to repeat its preparation, but were unable to do so. We can confirm Burian's statement that carbon dioxide is liberated in the reaction, but find the yield of this to be only about 40 per cent. of the theoretical, much less than he states. Moreover, we have isolated in a yield of about 30 per cent. of the theoretical the condensation product of diazobenzene-*p*-sulphonic acid and glyoxaline-4:5-dicarboxylic acid, namely, 2-*p*-sulphobenzeneazoglyoxaline-4:5-dicarboxylic acid (XX). No other definite compound could be isolated from the reaction mixture, and it appears to us that the compound described by Burian was probably a mixture of our acid with its sodium salt.

2-*p*-Sulphobenzeneazoglyoxaline-4:5-dicarboxylic acid yields on

oxide, probably owing to the formation of a disodium salt in solution. Moreover, the addition of alcohol to a solution of the acid in sufficient aqueous sodium hydroxide to form the disodium salt causes the precipitation of a granular deposit approximating in composition to the disodium salt. (Found, in salt dried at  $110^{\circ}$ , Na = 21.2.  $C_3H_2O_4N_2Na_2$  requires Na = 23.0 per cent.)

The acid is very stable towards nitric acid; after boiling it with ten times its weight of concentrated nitric acid for twenty-four hours, more than 90 per cent. was recovered unchanged, whilst similar results were obtained in a sealed tube at  $130^{\circ}$ , and when the acid was boiled with equal parts of nitric and sulphuric acids.

The acid is very resistant to esterification, for, after boiling with alcoholic sulphuric acid for twenty-four hours, 95 per cent. was recovered unchanged.

#### *The Preparation of Glyoxaline.*

One hundred grams of glyoxaline-4:5-dicarboxylic acid were distilled, under normal pressure, in quantities of 4 grams from a small flask into a long, wide air condenser. The distillate, which had solidified in the condenser, was crystallised from benzene, and gave a 92 per cent. yield of the pure base.

*Glyoxaline picrate* crystallises from water in long, fine, yellow needles, which become orange on drying at  $100^{\circ}$ , and then melt at  $212^{\circ}$  (corr.), after sintering from  $208^{\circ}$ . It contains rather more than  $1H_2O$  (Found, loss at  $100^{\circ}$  = 7.2; in substance dried at  $100^{\circ}$ , N = 23.3.  $C_3H_4N_2 \cdot C_6H_3O_7N_3$  [297.1] requires N = 23.6 per cent.).

*Glyoxaline hydrogen tartrate* crystallises from water in fine prisms of characteristic trapezoidal shape, which are anhydrous and melt at  $202^{\circ}$  (corr.). It is readily soluble in cold water, and is best crystallised from 50 per cent. alcohol (Found: N = 12.8.  $C_3H_4N_2 \cdot C_4H_6O_6$  [218.1] requires N = 12.8 per cent.).

Glyoxaline hydrogen oxalate crystallises from water as a felted mass of prismatic needles, which are anhydrous and melt at  $232^{\circ}$  (corr.) after sintering from  $230^{\circ}$ . It is soluble in five or six parts of boiling water, but much less so in cold water (Found: N = 17.8. Calc.: N = 17.7 per cent.).

#### *Action of Boiling Aniline on Glyoxaline-4:5-dicarboxylic Acid: Formation of Glyoxaline-4-carboxyanilide and Glyoxaline.*

Five grams of glyoxaline-4:5-dicarboxylic acid were boiled with 50 c.c. of aniline for nine hours under a reflux condenser, when

the acid gradually passed into solution. The product was mixed with water and subjected to distillation with steam until the excess of aniline had been removed. The residual aqueous solution was filtered from a small quantity of resinous matter whilst still hot, when the filtrate at once began to deposit the anilide as a felted mass of fine needles. The first crop amounted to 2.6 grams, and a further quantity of 0.1 gram was obtained on concentrating the mother liquor. The filtrate from this gave on acidification 0.1 gram of glyoxaline-4:5-dicarboxylic acid, but no glyoxaline-4-carboxylic acid was found. The final mother liquor when mixed with sodium carbonate, evaporated to dryness, and extracted with benzene gave 0.9 gram of glyoxaline.

*Glyoxaline-4-carboxyanilide* crystallises from boiling water in fine, colourless needles, which are anhydrous and melt at 227—228° (corr.). It is fairly readily soluble in alcohol, but only sparingly so in boiling water and the other usual organic solvents.

Found: C=64.2; H=5.1; N=22.6.

$C_{10}H_9ON_3$  (187.15) requires C=64.2; H=4.9; N=22.5 per cent.

*Hydrolysis of the Anilide.*—The anilide is only slowly hydrolysed by 10 per cent. hydrochloric acid at 100°, but more readily at 130°.

One gram of the anilide was heated with 10 c.c. of 10 per cent. hydrochloric acid at 130° for three hours. The resulting solution was evaporated to dryness to remove the excess of acid, the residue dissolved in water, basified with sodium carbonate, and extracted with ether to remove aniline. Sufficient hydrochloric acid was added to render the solution faintly acid to methyl-orange, when crystallisation set in almost immediately, and 0.42 gram of glyoxaline-4-carboxylic acid was isolated. The properties of the acid and its hydrochloride, nitrate, and picrate agreed with those previously given (T., 1916, 109, 199) for the acid prepared by the oxidation of 4-hydroxymethylglyoxaline, and the melting points of mixtures of the compounds from the two sources were not depressed.

#### *2-Methylglyoxaline-4:5-dicarboxylic Acid.*

This acid was prepared in an analogous manner to its lower homologue, employing a solution of 15 c.c. of freshly distilled acetaldehyde dissolved in 50 c.c. of ice-water in the place of the aqueous formaldehyde. The yield of 2-methylglyoxaline-4:5-dicarboxylic acid, containing  $1H_2O$ , obtained from 25 grams of tartaric acid was 22 grams, that is, 67 per cent. of the theoretical.

Maquenne (*loc. cit.*) obtained 50 grams of the product from 100 grams of tartaric acid, that is, 38 per cent. of the theoretical.

Generally, the properties of this acid are very similar to those of glyoxaline-4:5-dicarboxylic acid, and it behaves similarly on acid and alkaline hydrolysis.

With sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate, it gives a faint red colour which deepens on keeping, whilst glyoxaline-4:5-dicarboxylic acid gives a deeper red colour in the first instance.

*Action of Boiling Aniline on 2-Methylglyoxaline-4:5-dicarboxylic Acid.*

Twenty grams of hydrated 2-methylglyoxaline-4:5-dicarboxylic acid, when treated with boiling aniline under the same conditions as its lower homologue, gave 11 grams of the hydrated anilide of 2-methylglyoxaline-4-carboxylic acid and 3.8 grams of 2-methylglyoxaline.

2-Methylglyoxaline-4-carboxyanilide crystallises from boiling water as a felted mass of colourless, silky needles, which contain rather less than  $1\text{H}_2\text{O}$ . It is sparingly soluble in boiling water, but readily so in alcohol. After drying at  $110^\circ$ , it melts at  $208^\circ$  (corr.).

Found, loss at  $110^\circ$  in three samples = 6.9, 7.0, 7.2.

$\text{C}_{11}\text{H}_{11}\text{ON}_3 \cdot \text{H}_2\text{O}$  requires  $\text{H}_2\text{O}$  = 8.2 per cent.

Found, in substance dried at  $110^\circ$ , C = 65.1, 65.6; H = 5.7, 5.6; N = 20.9.

$\text{C}_{11}\text{H}_{11}\text{ON}_3$  (201.2) requires C = 65.6; H = 5.5; N = 20.9 per cent.

2-Methylglyoxaline-4-carboxylic acid is obtained in nearly the theoretical yield by the hydrolysis of its anilide under similar conditions to those already described for glyoxaline-4-carboxylic acid. When placed in a bath at  $250^\circ$ , it melts and effervesces at  $262^\circ$  (corr.). It crystallises from water in clusters of prismatic needles containing  $1\text{H}_2\text{O}$ . It is soluble in about twenty parts of boiling water, but is practically insoluble in the usual organic solvents.

Found, loss at  $110^\circ$  = 12.9.

$\text{C}_5\text{H}_6\text{O}_2\text{N}_2 \cdot \text{H}_2\text{O}$  requires  $\text{H}_2\text{O}$  = 12.5 per cent.

Found, in the substance dried at  $110^\circ$ , C = 47.3; H = 4.8; N = 21.9.

$\text{C}_5\text{H}_6\text{O}_2\text{N}_2$  (126.1) requires C = 47.6; H = 4.8; N = 22.2 per cent.

With sodium diazobenzene-*p*-sulphonate it gives a red colour in sodium carbonate solution.

The hydrochloride crystallises from water, in which it is readily

soluble, in minute, flattened, rhombic prisms, which are anhydrous. It melts and effervesces at  $268^{\circ}$  (corr.).

Found:  $N=16.9$ ;  $Cl=21.5$ .

$C_5H_6O_2N_2.HCl$  (162.6) requires  $N=17.2$ ;  $Cl=21.8$  per cent.

The *nitrate* crystallises from water, in which it is very readily soluble, in minute rhombic prisms, which melt and effervesce at  $190^{\circ}$  (corr.), resolidify, and on further heating gradually darken, melting at about  $240^{\circ}$ .

Found:  $C=31.7$ ;  $H=4.1$ .

$C_5H_6O_2N_2.HNO_3$  (189.1) requires  $C=31.7$ ;  $H=3.7$  per cent.

The *picrate* crystallises from water in minute cubes containing  $2H_2O$ , which is lost at  $100^{\circ}$  (Found:  $H_2O=9.4$ . Calc. for  $2H_2O$ ,  $9.2$  per cent.). It melts to a turbid liquid at  $200^{\circ}$  (corr.), which does not become clear until  $224^{\circ}$ , at which temperature effervescence begins.

Found, in salt dried at  $100^{\circ}$ ,  $N=19.4$ .

$C_5H_6O_2N_2.C_6H_5O_7.N_3$  (355.2) requires  $N=19.7$  per cent.

*2-Methylglyoxaline picrate* crystallises from boiling water in fine needles, which are anhydrous and melt at  $213^{\circ}$  (corr.).

Found:  $N=22.3$ .

$C_4H_6N_2.C_6H_5O_7.N_3$  (311.2) requires  $N=22.5$  per cent.

*2-Methylglyoxaline hydrogen oxalate* crystallises from water in large, rhombic prisms which contain  $2H_2O$  (Found:  $H_2O=17.6$ . Calc. for  $2H_2O$ :  $H_2O=17.3$  per cent.). After drying at  $100^{\circ}$ , it melts at  $160^{\circ}$  (corr.), and effervesces on further heating. It is much more readily soluble in water than the corresponding glyoxaline salt.

Found, in dried salt:  $N=16.1$ .

$C_4H_6N_2.C_2H_2O_4$  (172.1) requires  $N=16.3$  per cent.

#### *2-Ethylglyoxaline-4:5-dicarboxylic Acid.*

This acid was prepared in the same way as the methyl substituted acid. From 32 c.c. of propaldehyde, and the nitrotartaric acid obtained from 50 grams of tartaric acid, 43 grams of hydrated 2-ethylglyoxaline-4:5-dicarboxylic acid were obtained, that is, 64 per cent. of the theoretical yield; Maquenne obtained 30 per cent. 2-Ethylglyoxaline-4:5-dicarboxylic acid melts and effervesces at  $259^{\circ}$  (corr.).

*2-Phenylglyoxaline-4:5-dicarboxylic Acid.*

The nitrotartaric acid from 25 grams of tartaric acid was treated with 100 c.c. of aqueous ammonia in the manner previously described. Then 20 grams of benzaldehyde were added, with stirring, below  $0^{\circ}$ , and the stirring was continued for seven hours, the temperature of the mixture being gradually allowed to approach that of the room. After keeping overnight, 17.1 grams of 2-phenylglyoxaline-4:5-dicarboxylic acid were isolated, that is, 48 per cent. of the theoretical yield, whereas Maquenne's yield was only 8 per cent. 2-Phenylglyoxaline-4:5-dicarboxylic acid melts and effervesces at  $271^{\circ}$  (corr.).

When distilled under the conditions previously described in the case of glyoxaline-4:5-dicarboxylic acid, it gives 2-phenylglyoxaline in a yield of more than 80 per cent. of the theoretical.

2-Phenylglyoxaline crystallises from water in small, prismatic needles, which melt at  $148-149^{\circ}$  (corr.) and are anhydrous.

2-Phenylglyoxaline nitrate is readily soluble in water, but less so in alcohol, from which it separates in leaflets containing  $\frac{3}{4}\text{H}_2\text{O}$ , which is lost at  $60^{\circ}$  in a vacuum. The dried salt melts at  $135^{\circ}$  (corr.).

Found, in air-dried salt,  $\text{H}_2\text{O}=6.1$ ; in dried salt,  $\text{N}=20.0$ .

$\text{C}_9\text{H}_8\text{N}_2\cdot\text{HNO}_3$  (207.1) requires  $\text{N}=20.3$  per cent.

The *hydrogen oxalate* crystallises from water in flattened needles, which melt and effervesce at  $219^{\circ}$  (corr.), and are anhydrous. It is readily soluble in hot water, but less so in cold.

Found:  $\text{N}=12.0$ .

$\text{C}_9\text{H}_8\text{N}_2\cdot\text{C}_2\text{H}_2\text{O}_4$  (234.1) requires  $\text{N}=12.0$  per cent.

The *picrate* is sparingly soluble even in boiling water, from which it crystallises in fine needles which melt at  $238^{\circ}$  (corr.), and are anhydrous.

Found:  $\text{N}=18.6$ .

$\text{C}_9\text{H}_8\text{N}_2\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$  (373.2) requires  $\text{N}=18.8$  per cent.

*4:5-Dimethyl- and 2:4:5-Trimethyl-glyoxaline.*

When 4:5-dimethylglyoxaline is prepared by Windaus' method (*Ber.*, 1909, **42**, 758), it is contaminated with 2:4:5-trimethylglyoxaline, which results from the interaction of diacetyl and ammonia (von Pechmann, *Ber.*, 1888, **21**, 1414).

8.6 Grams of diacetyl were dissolved in 50 c.c. of water, 50 c.c. of 40 per cent. aqueous formaldehyde added, the mixture cooled to  $0^{\circ}$ , and 80 c.c. of concentrated ammonia solution gradually



added, the reaction mixture being stirred and kept below  $0^{\circ}$ . After the addition was ended, the mixture was allowed to remain in a cool place overnight, then evaporated to a low bulk, saturated with anhydrous potassium carbonate, and the oil which separated extracted by ether. The crude extract, which was contaminated with hexamine, amounted to 5.9 grams. After destruction of the hexamethylenetetramine by boiling dilute hydrochloric acid, the picrates of the constituent bases were fractionated from water, when 5.7 grams of 4:5-dimethylglyoxaline picrate (17.5 per cent. of the theoretical yield) were obtained first, and then 3.5 grams of 2:4:5-trimethylglyoxaline picrate.

2:4:5-Trimethylglyoxaline picrate sinters from  $160^{\circ}$  and melts at  $163^{\circ}$  (corr.). It crystallises from water in well-defined prisms, which are often serrated.

Found: N=20.6.

$C_6H_{10}N_2, C_6H_5O_7N_3$  requires N=20.6 per cent.

The hydrochloride, previously prepared by von Pechmann, crystallises from alcohol in fine needles, which are anhydrous and melt at  $316^{\circ}$  (corr.) (Found: N=19.0; Cl=24.2. Calc.: N=19.1; Cl=24.2 per cent.).

4:5-Dimethylglyoxaline hydrochloride crystallises from alcohol in well-defined, rhombic prisms which melt and decompose at  $305^{\circ}$  (corr.).

Found: N=21.1; Cl=26.4.

$C_5H_8N_2.HCl$  requires N=21.1; Cl=26.7 per cent.

4:5-Dimethylglyoxaline was also prepared by a modification of Künne's method (*Ber.*, 1895, **28**, 2039; compare also Jowett, T., 1905, **87**, 407). Nine grams of methyl  $\alpha$ -isonitrosoethyl ketone were reduced with stannous chloride, as described by Künne, but the temperature of the reaction mixture was maintained at  $15^{\circ}$ , and, after the removal of the tin, the evaporation of the liquor was conducted entirely under diminished pressure. By these means, a yield of 10 grams of crude, crystalline methyl  $\alpha$ -aminoethyl ketone hydrochloride was obtained, as against 4.2 grams of syrup obtained by Künne. When this product was heated on the water-bath for four hours with 10 grams of potassium thiocyanate and 40 c.c. of water, 5.2 grams of 2-thiol-4:5-dimethylglyoxaline separated, and this gave 4:5-dimethylglyoxaline picrate in a yield of 85 per cent. of the theoretical when oxidised with the calculated quantity of ferric chloride.\* The yield of 4:5-dimethylglyoxaline from methyl ethyl ketone is thus 23.8 per cent. of the theoretical.

\* The method of oxidising thiolglyoxalines to glyoxalines by means of ferric chloride has been described by one of us (T., 1911, **99**, 2175) in the case of

*Part II. Nitroglyoxalines.**4-Nitroglyoxaline.*

Rung and Behrend (*loc. cit.*) prepared 4-nitroglyoxaline in a yield of 36 per cent. of the theoretical by boiling glyoxaline with a mixture of nitric and sulphuric acids. The yield can be improved greatly by the method given below. Eight grams of glyoxaline were dissolved in 16 c.c. of nitric acid (D 1.4), cooled, and 16 c.c. of sulphuric acid cautiously added. A vigorous reaction ensued, and when this had subsided the mixture was boiled gently for two hours, allowed to cool, and then poured into ice-water, when 7.85 grams of 4-nitroglyoxaline separated. The mother liquors yielded a further 0.5 gram of 4-nitroglyoxaline identical with the above, but no glyoxaline and merely a trace of other crystalline material. The total yield of 4-nitroglyoxaline thus amounted to 63 per cent. of the theoretical. 4-Nitroglyoxaline crystallises from boiling acetic acid or from alcohol in stout, rhombic prisms, which are anhydrous and melt at 312—313° (corr.) (Found: N=36.8. Calc.: N=37.1 per cent.). It is only very sparingly soluble in boiling water. Although it dissolves in strong mineral acids, it is precipitated unchanged on the addition of water, and is recovered unchanged when crystallised from aqueous picric acid.

4-Nitro-2-methylglyoxaline was similarly prepared. It crystallises from water in fine needles, which are anhydrous and melt at 254° (corr.), sintering from 251°.

Found: N=33.0.

$C_4H_5O_2N_3$  (127.1) requires N=33.1 per cent.

5-Nitro-4-methylglyoxaline was prepared by Windaus (*loc. cit.*) in a 60 per cent. yield by warming 4-methylglyoxaline with fuming nitric acid at 80°. Using this method, we found the main product to be 4-methylglyoxaline nitrate. Proceeding according to the method described for 4-nitro-2-methylglyoxaline, 5 grams of 4-methylglyoxaline gave 7 grams of 5-nitro-4-methylglyoxaline (Found: N=32.8. Calc.: N=33.1 per cent.) melting at 248° (corr.), that is, 90 per cent. of the theoretical yield.

2-thiol-4-aminomethylglyoxaline. The low yield of 4-aminomethylglyoxaline recorded (56 per cent. of the theoretical) was due to the fact that insufficient ferric chloride had been employed. When the calculated quantity (16.2 grams) of this reagent is used, the product is obtained in a yield of 90 per cent. of the theoretical.

*Attempted Nitration of 4:5-Dimethylglyoxaline.*

To five grams of 4:5-dimethylglyoxaline dissolved in 15 c.c. of nitric acid (D 1.4), 15 c.c. of sulphuric acid were added. The first vigorous reaction was controlled by cooling, and after it had ended the mixture was heated for two hours on the water-bath. From the reaction product, 1.7 grams of 4:5-dimethylglyoxaline were recovered, together with 0.3 gram of the nitrate of 4-methylglyoxaline-5-carboxylic acid (Found: C=32.1; H=4.0; N=21.7. Calc.: C=31.6; H=3.7; N=22.1 per cent.), which deposited the corresponding acid, melting and effervescing at 222°, on the addition of the calculated quantity of sodium hydroxide. From the pure acid, the hydrochloride, which melted and decomposed at 231°, and the nitrate, which decomposed at 189°, were prepared. The melting points of the acid and its salts are in agreement with those found by Gerngross (*loc. cit.*) for 4-methylglyoxaline-5-carboxylic acid.

*Reduction of Nitroglyoxalines with Tin and Hydrochloric Acid.*

When 4-nitroglyoxaline, 4-nitro-2-methylglyoxaline, or 5-nitro-4-methylglyoxaline is reduced with tin and hydrochloric acid, and the product mixed with sodium hydroxide and distilled into standard acid, two of the three atoms of nitrogen present in the molecule are eliminated in the form of ammonia:

0.5609 of 4-nitroglyoxaline gave 0.1746 NH<sub>3</sub>; calc. as above, 0.1688.

0.4292 of 4-nitro-2-methylglyoxaline gave 0.118 NH<sub>3</sub>; calc. as above, 0.115.

0.4931 of 5-nitro-4-methylglyoxaline gave 0.1378 NH<sub>3</sub>; calc. as above, 0.1320.

That the greater part of the ammonia is actually produced during the reduction, and not by the subsequent action of the alkali, is shown in the case of 4-nitroglyoxaline by the following experiment.

Twelve grams of 4-nitroglyoxaline were reduced by means of tin and hydrochloric acid in the usual manner. The reduced liquors were freed from tin and then evaporated to dryness, then moistened with alcohol, and again evaporated to remove water as far as possible. The crude product was extracted with alcohol and left 9 grams of a crystalline solid, which proved to be ammonium chloride (Found: N=25.9; Cl=66.0. Calc.: N=26.2;

Cl=66.3 per cent.). The residue of the purple alcoholic solution gave 5 grams of an insoluble phosphotungstate after the removal of ammonia. This product has not yet been investigated.

*Reduction of Nitroglyoxalines with Sodium Hyposulphite.*

Behrend and Schmitz (*loc. cit.*) observed that 4-nitroglyoxaline gave a beautiful blue dye when treated with alkaline reducing agents. We can confirm this result, but find that ammonia is also produced in an amount corresponding with the loss of two atoms of nitrogen in this form from three molecules of 4-nitroglyoxaline when this compound is reduced with sodium hyposulphite in aqueous sodium hydroxide:

0.5148 of 4-nitroglyoxaline gave 0.0521  $\text{NH}_3$ ; calc. as above, 0.0516.

The liquors remaining from the distillation gradually acquired a dark blue colour on exposure to the air, and on acidification with acetic acid deposited rather less than 0.1 gram of a blue compound which did not melt below  $300^\circ$ .

The reduction of 5-nitro-4-methylglyoxaline with alkaline sodium hyposulphite led to the same result as in the case of 4-nitroglyoxaline, two molecules of ammonia being produced from three molecules of the nitro-compound (0.5311 gave 0.0487  $\text{NH}_3$ ; calc. as above, 0.0474). The reduced solution gradually acquired a rose colour on exposure to air, but gave no precipitate with acetic acid.

4-Nitro-2-methylglyoxaline behaved differently from the above compounds on reduction with alkaline sodium hyposulphite, yielding one molecule of ammonia from three molecules of the nitro-compound (0.5084 gave 0.0230  $\text{NH}_3$ ; calc. as above, 0.0227).

*Part III. Arylazoglyoxalines.*

*2-Benzeneazoglyoxaline (IV, p. 221).*

23.25 Grams of aniline were dissolved in 62.5 c.c. of hydrochloric acid and 187.5 c.c. of water, and diazotised with 18 grams of sodium nitrite dissolved in 100 c.c. of water. The solution was run slowly into a well-stirred solution of 17 grams of glyoxaline and 40 grams of anhydrous sodium carbonate in 1250 c.c. of water, previously cooled to  $5^\circ$ , and kept overnight. The insoluble orange powder was collected, washed well with water, and extracted successively with 250, 125, and 125 c.c. of cold 2.5 per cent. hydrochloric acid. (Extract=A.) The insoluble material amounted to 4.4

grams, and after crystallisation from alcohol gave 2:4:5-*tris-benzeneazoglyoxaline*, of which only 0.5 gram was obtained in a pure state. This compound decomposes at about 200° and effervesces at 208° (corr.). When pure, it is only sparingly soluble even in boiling alcohol, from which it crystallises slowly in dark brown clusters of crystals of indeterminate shape. (0.84 required 60 c.c. of boiling alcohol.)

Found: C=66.0; H=4.6; N=29.0.

$C_{21}H_{16}N_8$  (380.3) requires C=66.3; H=4.2; N=29.5 per cent.

Trisbenzeneazoglyoxaline is insoluble in cold dilute hydrochloric acid, and is decomposed when boiled with this reagent. It dissolves to some extent in aqueous sodium hydroxide.

The hydrochloric acid extract (d) was diluted with water and basified with sodium carbonate, when crude 2-benzeneazoglyoxaline was obtained as a yellow, crystalline precipitate, which, after thorough washing with cold water and drying, amounted to 34 grams. On crystallisation from 150 c.c. of alcohol, 31 grams of the pure base were obtained, that is, 74 per cent. of the theoretical. No other definite compound could be isolated from the mother liquor.

2-Benzeneazoglyoxaline crystallises from alcohol in large, orange tablets resembling potassium dichromate in appearance. It melts at 190° (corr.) to a reddish-black liquid.

Found: C=62.7, 62.7; H=4.8, 4.9; N=32.3

$C_9H_8N_4$  (172.1) requires C=62.8; H=4.7; N=32.6 per cent.

*Rung and Behrend's Method.*—By this method, in which benzene-diazonium chloride is allowed to react with glyoxaline without the addition of alkali, 5 grams of glyoxaline gave 3.3 grams of crude precipitate insoluble in water. Of this, 2.2 grams were separated into 0.7 gram of insoluble resin, which appeared to evolve gas on keeping, and 1.45 grams soluble in acid, which gave pure 2-benzeneazoglyoxaline on crystallisation from alcohol. The crude precipitate was less readily purified by direct crystallisation from alcohol.

*General Properties of Arylazoglyoxalines.*—To avoid repetition, it will be convenient to describe the general properties of the monoarylazoglyoxalines at this point. 2-Benzeneazoglyoxaline and 2-benzeneazo-4-methylglyoxaline are fairly readily soluble in alcohol, ethyl acetate, or acetone, sparingly so in ether, chloroform, or benzene. 5-Benzeneazo-4-methylglyoxaline, 2-*p*-bromobenzeneazoglyoxaline, and 4-*p*-bromobenzeneazo-2-methylglyoxaline are sparingly soluble in the first three solvents and very sparingly so in the last three.

These compounds are almost insoluble in cold water or in dilute aqueous ammonia or sodium carbonate, but dissolve to some extent in dilute aqueous sodium hydroxide. The benzeneazo-compounds dissolve readily in dilute hydrochloric acid, and the solutions yield crystalline hydrochlorides on concentration; the hydrochlorides of the *p*-bromobenzeneazo-compounds are sparingly soluble in water.

The stability of a 2- and a 4-substituted member of the group towards boiling dilute hydrochloric acid was examined. When 0.5 gram of 2-benzeneazoglyoxaline was boiled with 20 c.c. of 10 per cent. aqueous hydrochloric acid for two hours under a reflux condenser, 0.35 gram was recovered little changed on the addition of ammonia, and readily gave the starting material in a pure state on crystallisation from alcohol.

When 5-benzeneazo-4-methylglyoxaline was boiled with an excess of 10 per cent. aqueous hydrochloric acid for a few minutes, it was recovered unchanged after the addition of ammonia, but after boiling for one hour it was mainly decomposed, with the formation of resinous compounds.

The arylazoglyoxalines dissolve in concentrated sulphuric acid, giving bright-coloured solutions. The monoaryloazo-derivatives yield mainly orange or magenta solutions, the 2-substituted derivatives being more intensely coloured than the 4-substituted compounds, whilst the solutions of bis- and tris-arylazoglyoxalines are green and still more intense than those of the 2-monoaryloazo-derivatives.

*Reduction of 2-Benzeneazoglyoxaline with Stannous Chloride:  
Isolation of 2-Amino-4-p-aminophenylglyoxaline, 2-Amino-  
glyoxaline, Guanidine, and Aniline.*

Twenty grams of 2-benzeneazoglyoxaline were dissolved in 200 c.c. of boiling 2.5 per cent. hydrochloric acid and mixed with 120 c.c. of stannous chloride solution.\* The solution was immediately decolorised, and when mixed with 200 c.c. of hydrochloric acid deposited a crystalline tin salt (A). This was collected, and the mother liquor was evaporated to dryness, dissolved in hot water, and freed from tin. It was then evaporated to low bulk, mixed with sodium carbonate, and extracted with ether, which removed 3.0 grams of crude aniline. The alkaline liquor was acidified faintly with hydrochloric acid, evaporated to dryness, and extracted with alcohol, when 3.1 grams of extract were obtained. This was

\* The stannous chloride solution employed throughout this investigation was made by mixing 40 grams of "tin salt" with sufficient hydrochloric acid to make 100 c.c. of solution.

mixed with stannic chloride, and deposited, first, 2.2 grams of pure 2-aminoglyoxaline stannichloride, then crops of the crude salt, from which a further quantity of 1.0 gram of the pure salt was obtained, the total yield amounting to 11 per cent. of the theoretical. The final stannichloride mother liquors were deprived of tin by means of hydrogen sulphide and mixed with picric acid. After crystallisation from water, the first crop of picrate, which melted at 325°, was decomposed by sulphuric acid, the picric acid being removed by means of ether. The solution of sulphates was deprived of sulphuric acid by barium hydroxide, and from excess of this reagent by carbon dioxide. The resulting solution was neutralised with aqueous oxalic acid, mixed with as much more aqueous oxalic acid, and concentrated, when crude guanidine hydrogen oxalate separated. After recrystallisation from water, this amounted to 0.07 gram, melting and effervescing at 172—173° (corr.) alone or when mixed with pure guanidine hydrogen oxalate.

The crystalline tin salt (A) was dissolved in water, treated with hydrogen sulphide, filtered from tin sulphide, and concentrated, when 18.55 grams of 2-amino-4-p-aminophenylglyoxaline dihydrochloride separated, that is, 64.6 per cent. of the theoretical yield.

*2-Amino-4-p-aminophenylglyoxaline*,  $C_9H_{10}N_4$  (VI, p. 222).

When the dihydrochloride is mixed with an equivalent quantity of sodium carbonate, a colourless oil separates which solidifies on keeping. This is a carbonate, for it effervesces on treatment with acid, and when dissolved in boiling water disengages carbon dioxide vigorously on the addition of animal charcoal, leaving a solution of the free base, which crystallises on keeping. This solution becomes brown at the top owing to oxidation in the air, whilst the laminæ become mauve where exposed to the light.

To 5.0 grams of the dihydrochloride in 50 c.c. of boiling water, 30 c.c. of hot 10 per cent. aqueous sodium carbonate and a pinch of animal charcoal were added. The solution was boiled for five minutes, filtered, and kept, when 3.1 grams of the base separated and were recrystallised from water. This base crystallises from water in glistening leaflets which melt and effervesce at 148° (corr.). It contains  $1H_2O$ , which is not lost in a vacuum or on heating at 100°.

Found: C=56.3; H=6.4; N=29.5, 29.2.

$C_9H_{10}N_4 \cdot H_2O$  (192.2) requires C=56.2; H=6.3; N=29.2 per cent.

It is sparingly soluble in cold, fairly readily so in hot water; fairly readily soluble in cold, readily in hot alcohol, and very sparingly so in chloroform or ether.

An aqueous solution of the base gives, with silver nitrate, a white precipitate, which blackens at once on the addition of ammonia; with Fehling's solution, a nearly black precipitate—presumably a copper salt—which is unchanged on boiling the solution; with cold permanganate, instant reduction; with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate, an immediate cherry-red colour. When the base is dissolved in an excess of hydrochloric acid and mixed with sodium nitrite, a yellow solution is obtained, which yields with a solution of  $\beta$ -naphthol in aqueous sodium hydroxide a sparingly soluble purple dye. On the addition of sodium hydroxide to a solution containing 2-amino-4-*p*-aminophenylglyoxaline hydrochloride and sodium nitroprusside, a green coloration changing to chestnut-brown is produced.

On the addition of dilute sulphuric acid to an aqueous solution of the base or its hydrochloride, the very sparingly soluble sulphate crystallises in woolly needles.

The *dihydrochloride* crystallises from dilute hydrochloric acid in colourless prisms, which do not melt below  $300^{\circ}$ . It is readily soluble in cold, very readily so in hot water.

Found: Cl=28.6; N=22.5.

$C_9H_{10}N_4 \cdot 2HCl$  (247.1) requires Cl=28.7; N=22.7 per cent.

The *dipicrate* forms yellow, silky needles, which darken at  $245^{\circ}$  and decompose at  $250^{\circ}$  (corr.). It is very sparingly soluble even in boiling water.

The benzylidene derivative of 2-amino-4-*p*-aminophenylglyoxaline was not obtained in a crystalline form.

#### *2-Acetylamino-4-p-acetylaminophenylglyoxaline.*

10.6 Grams of 2-amino-4-*p*-aminophenylglyoxaline were boiled with 50 c.c. of acetic anhydride for one hour under a reflux condenser and mixed with aqueous sodium carbonate, when 13.9 grams of the diacetyl derivative were obtained, that is, 98 per cent. of the theoretical yield. The base forms a colourless, crystalline powder which does not melt below  $300^{\circ}$ .

Found: N=21.2.

$C_{13}H_{14}O_2N_4$  (258.2) requires N=21.7 per cent.

It dissolves in dilute hydrochloric acid, but the hydrochloride crystallises almost at once. It appears to be changed by prolonged boiling with hydrochloric acid.

The *hydrochloride* was consequently prepared by triturating the base with an excess of 10 per cent. aqueous hydrochloric acid, draining the insoluble salt, and crystallising it from water, when it



formed colourless, prismatic needles, which did not melt below 300°. It is sparingly soluble in cold, fairly readily so in hot water.

Found, in air-dried salt, loss at 110° = 11.1.

$C_{13}H_{14}O_2N_4 \cdot HCl \cdot 2H_2O$  (330.7) requires  $2H_2O = 10.9$  per cent.

Found, in salt dried at 110°, C = 53.1; H = 5.3; N = 18.7; Cl = 11.6.

$C_{13}H_{14}O_2N_4 \cdot HCl$  (294.7) requires C = 53.0; H = 5.1; N = 19.0; Cl = 12.0 per cent.

*Oxidation.*—Ten grams of 2-acetyl-amino-4-*p*-acetylaminophenyl-glyoxaline were suspended in 150 c.c. of cold water and mixed with 4 grams of 50 per cent. aqueous sulphuric acid, when a suspension of the sulphate resulted. To this, cold 4 per cent. aqueous potassium permanganate was added until a test portion of the product remained pink for a few seconds, about 240 c.c. being required. The liquor was then filtered from manganese hydroxide, acidified with hydrochloric acid, and extracted with ether. The ethereal extract amounted to 1.5 grams, and after digestion with a little warm water left 1.0 gram of *p*-acetylaminobenzoic acid, which melted at 260° (corr.). After recrystallisation from boiling water, the acid formed glistening needles having the same melting point. A specimen of the pure acid from another source and a mixture of the two melted at the same temperature. The identification was confirmed by analysis (Found: C = 59.9; H = 5.2; N = 7.8. Calc.: C = 60.3; H = 5.1; N = 7.8 per cent.) and by hydrolysis to *p*-aminobenzoic acid, which melted at 190° (corr.) alone or mixed with the acid resulting from the reduction of *p*-nitrobenzoic acid.

*Reduction of 2-Benzeneazoglyoxaline with Zinc Dust and Acetic Acid: Isolation of Glycocyamidine, Aniline, and 2-Amino-4-*p*-aminophenylglyoxaline.*

To a boiling solution of 17.2 grams of 2-benzeneazoglyoxaline in 100 c.c. of glacial acetic acid and 300 c.c. of water, 45 grams of zinc dust were added gradually in the course of twenty minutes without further heating. The excess of zinc was removed, the liquor diluted with 2 litres of water, giving an indigo-coloured solution, and treated with hydrogen sulphide. After collecting the zinc sulphide—which had carried down the colouring matter—the liquor was mixed with 20 c.c. of hydrochloric acid and evaporated to dryness. The residue was dissolved in a little water, mixed with sodium carbonate, and extracted with ether, when 2.7 grams of insoluble, black material were deposited; this contained zinc

carbonate and the carbonate of 2-amino-4-*p*-aminophenylglyoxaline. The ethereal extract left on evaporation 7.0 grams of practically pure aniline. The alkaline liquor was acidified faintly with hydrochloric acid, mixed with a solution of 23 grams of picric acid in 1 litre of boiling water, and stirred, when 2.6 grams of 2-amino-4-*p*-aminophenylglyoxaline dipicrate separated immediately as a brownish-yellow, crystalline powder which melted at 240°; for the identification of this substance, the hydrochloride and base were prepared and found to have the properties recorded above.

The filtrate from this salt was kept overnight, when 21.5 grams of a granular, crystalline picrate, melting at 196°, separated, and on concentrating the mother liquor a further 4.8 grams, melting at 180°, were obtained. These crops were mixed, converted into the hydrochloride, and crystallised from alcohol, when eventually 5.9 grams of pure glycoeyamidine hydrochloride were obtained, that is, 43 per cent. of the theoretical yield. It formed clusters of prismatic needles, which began to darken and sinter at 205° and melted at 211–213° (corr.). E. Schmidt (*Arch. Pharm.*, 1913, 251, 557) states that it begins to discolour at 200° and melts at 208–210° (Found: C=26.5; H=4.4; N=30.6; Cl=26.3.  $C_3H_5ON_3.HCl$  (135.6) requires C=26.6; H=4.5; N=31.0; Cl=26.2 per cent.).

To complete the identification of this compound, the base and some other salts were prepared. The base crystallised from water in colourless, prismatic needles, which began to darken slowly from about 220° and quickly from about 250°, without melting even at 300°. It was anhydrous. (Found: C=36.4; H=4.8; N=42.3.  $C_3H_5ON_3$  (99.1) requires C=36.3; H=5.1; N=42.4 per cent.) E. Schmidt (*loc. cit.*) states that glycoeyamidine darkens from 220°, but does not melt at 250°. It gave with sodium nitroprusside and sodium hydroxide an orange solution, which became Burgundy-red on the addition of acetic acid (Weyl's reaction). It is stable towards cold aqueous permanganate in acid solution, but reduces cold alkaline permanganate, yielding a green solution.

The platinichloride was obtained on spontaneous evaporation of an aqueous solution in large, transparent, quadrilateral tablets having the composition  $C_3H_5ON_3.H_2PtCl_6.2H_2O$ . It begins to darken at 220°, gradually sinters, and is quite black by 260° without actually melting even at 300°. E. Schmidt (*loc. cit.*) found that glycoeyamidine platinichloride had this composition and did not melt at 260°, but sintered and blackened earlier.

The platinichloride was also obtained in an anhydrous form by crystallisation from a hot concentrated solution, when it formed clusters of prisms.

The additive compound with gold chloride,  $C_9H_6ON_3AuCl_3$ , melted at  $157-158^\circ$  (corr.). Korndörfer (*Arch. Pharm.*, 1904, **242**, 633) found that glycoeyamidine gold chloride had this composition, and melted at  $153-154^\circ$ .

The picrate crystallised from water in glistening, striated, yellow leaflets (flat needles) which melted at  $215-216^\circ$  (corr.). Jaffé (*Zeitsch. physiol. Chem.*, 1906, **48**, 430) describes glycoeyamidine picrate as forming needles, which melt at  $210^\circ$ .

*2- and 4-p-Bromobenzeneazoglyoxaline.*

34.4 Grams of *p*-bromoaniline in 200 c.c. of hydrochloric acid and 600 c.c. of water were diazotised at  $-2^\circ$  to  $0^\circ$  by a solution of 14.4 grams of sodium nitrite in 72 c.c. of water. The solution was kept for twenty minutes and poured in a slow stream into a solution of 13.6 grams of glyoxaline and 300 grams of sodium carbonate crystals in 2 litres of water, previously cooled to  $5^\circ$ . After adding a little more aqueous sodium carbonate, the mixture was kept overnight, and the insoluble, yellow powder collected and washed with water. It amounted to 48.7 grams after drying in the air, decomposed at  $245^\circ$ , and was almost completely soluble in dilute hydrochloric acid. After fractional crystallisation from alcohol, there were obtained 37.5 grams of pure 2-*p-bromobenzeneazoglyoxaline* and 5.1 grams scarcely less pure, whilst the final mother liquors deposited a mixture of this compound with dark brown warts, which were separated mechanically, and amounted to about 2.5 grams, melting at about  $175^\circ$ . These were dissolved in dilute hydrochloric acid, and the solution was filtered from a little dark brown, insoluble matter and mixed with ammonia, when a yellow, gelatinous precipitate was formed, which readily became crystalline on warming and stirring. This base was collected and crystallised several times from alcohol, when 4-*p-bromobenzeneazoglyoxaline* was obtained in a pure state.

2-*p-Bromobenzeneazoglyoxaline* crystallises from alcohol in chestnut-brown, prismatic needles, which melt and decompose at  $253^\circ$  (corr.).

Found: C=42.9; H=3.1; N=22.1.

$C_9H_7N_4Br$  (251.1) requires C=43.0; H=2.8; N=22.3 per cent.

4-*p-Bromobenzeneazoglyoxaline* crystallises from alcohol in clusters of brownish-yellow prisms which melt and decompose at  $191^\circ$  (corr.).

Found: C=43.2; H=3.1; N=21.9.

$C_9H_7N_4Br$  (251.1) requires C=43.0; H=2.8; N=22.3 per cent.

On reducing this base (0.26 gram) with stannous chloride and distilling the resulting solution with an excess of sodium hydroxide, the volatile products consisted of *p*-bromoaniline (0.18 gram) and ammonia, which gave 0.05 gram of ammonium chloride.

*Reduction of 2-p-Bromobenzeneazoglyoxaline with Stannous Chloride: Isolation of 2-Aminoglyoxaline, p-Bromoaniline, Guanidine, 2-Amino-4-p-aminophenylglyoxaline, and a Base, C<sub>9</sub>H<sub>9</sub>N<sub>4</sub>Br.*

To 78 grams of 2-*p*-bromobenzeneazoglyoxaline suspended in 40 c.c. of hydrochloric acid and 1 litre of boiling water, 400 c.c. of stannous chloride solution were added. The solution immediately became decolorised, and, after the removal of 0.5 gram of brown, insoluble matter, was concentrated under diminished pressure. The tin salts which separated were collected from time to time and combined, so that the product was obtained in two fractions, consisting of the crystalline tin salts and the syrupy residue.

The crystalline tin salts were dissolved in water and deprived of tin by hydrogen sulphide. The solution of hydrochlorides was evaporated to dryness, dissolved in a little water, and mixed with aqueous sodium carbonate, when 39.6 grams of *p*-bromoaniline separated. The filtrate from this gave a further 1.1 grams of the same compound on extraction with ether, and was next acidified with hydrochloric acid, evaporated to dryness, and extracted with absolute alcohol. (Insoluble material = A.) On distilling the alcohol, a brown syrup remained, which quickly crystallised and became a rock-like mass of 2-aminoglyoxaline hydrochloride, amounting to 15.8 grams and melting at 135—140°.

The syrupy tin salts were also dissolved in water and deprived of tin. The resulting solution was evaporated to dryness, dissolved in a little water, mixed with sodium carbonate, and extracted with ether. This, on concentration, deposited 0.9 gram of colourless needles, melting at 178° (corr.), which proved to be a *base* having the composition C<sub>9</sub>H<sub>9</sub>N<sub>4</sub>Br (compare p. 245). The ethereal mother liquor on evaporation left 2.5 grams of dark brown syrup which gradually crystallised, and consisted largely of *p*-bromoaniline.

The alkaline liquor was acidified with hydrochloric acid, evaporated to dryness under diminished pressure, and extracted with absolute alcohol. The insoluble salts, consisting mainly of sodium chloride, were combined with those obtained previously (A), dissolved in water, and mixed with aqueous picric acid, when 2.7 grams of 2-amino-4-*p*-aminophenylglyoxaline dipicrate, melt-

ing at  $240^{\circ}$ , separated; the identity of this salt was confirmed by its conversion into the hydrochloride and base. The alcoholic extract was evaporated under diminished pressure, and left 13.0 grams of brown syrup, which crystallised only partly on seeding with 2-aminoglyoxaline hydrochloride. It was converted into the stannichloride and crystallised fractionally from 10 per cent. hydrochloric acid, when 10.2 grams of 2-aminoglyoxaline stannichloride melting at  $280^{\circ}$  (corr.) were obtained. This is equivalent to 4.9 grams of 2-aminoglyoxaline hydrochloride, the total yield of which was therefore 20.7 grams, that is, 56 per cent. of the theoretical.

The remaining stannichlorides were not readily purified by fractional crystallisation, and were reconverted into hydrochlorides, which amounted to about 3 grams. This material was mixed with sodium carbonate, evaporated until nearly dry, and extracted with hot alcohol.\* The extract was distilled and the residue mixed with an excess of 10 per cent. aqueous oxalic acid, when 1.6 grams of guanidine hydrogen oxalate separated in large crystals. After recrystallisation from water, this salt formed colourless spears, which melted at  $173\text{--}174^{\circ}$  (corr.) after drying at  $100^{\circ}$ , and was sparingly soluble in water.

It had the composition  $\text{CH}_5\text{N}_3\text{C}_2\text{H}_2\text{O}_4\text{H}_2\text{O}$  previously recorded by Strecker (*Annalen*, 1861, 118, 160). (Found:  $\text{H}_2\text{O}=10.3$ . Calc.:  $\text{H}_2\text{O}=10.8$ . Found, in dried salt,  $\text{C}=24.0$ ;  $\text{H}=4.9$ ;  $\text{N}=28.0$ . Calc.:  $\text{C}=24.1$ ;  $\text{H}=4.7$ ;  $\text{N}=28.2$  per cent.) The melting point of a specimen of guanidine hydrogen oxalate prepared synthetically and that of a mixture of the two preparations was the same. The identification was confirmed by the preparation of the nitrate and picrate, which had the properties previously recorded.

The base, melting at  $178^{\circ}$  (corr.), obtained as a by-product in the above reaction (compare p. 244), forms colourless needles from alcohol or ether. It contains halogen. It is sparingly soluble in water, readily so in cold, and very easily soluble in hot alcohol, but sparingly so in ether. Its alcoholic solution gradually becomes purple when exposed to the air.

Found:  $\text{C}=43.0$ ;  $\text{H}=3.9$ ;  $\text{N}=21.9$ .

$\text{C}_9\text{H}_5\text{N}_4\text{Br}$  (253.1) requires  $\text{C}=42.7$ ;  $\text{H}=3.6$ ;  $\text{N}=22.1$  per cent.

0.122 Gram mixed with an excess of hydrochloric acid and evaporated to dryness gave 0.153 gram of salt, which is therefore

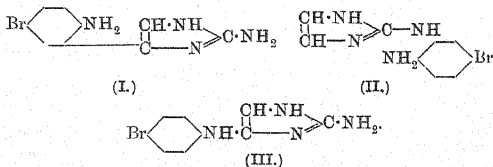
\* The method employed for the extraction of guanidine carbonate is unsuitable, and it is probable that a considerable proportion remained behind with the sodium carbonate.

a *dihydrochloride* (calc. yield, 0.157 gram). This salt crystallised from water in elongated leaflets, which, after drying at 100°, melted and decomposed at 245° (corr.) after sintering earlier. The (*di*)*picrate* crystallises from water in woolly needles, which melt at 225° (corr.), and are sparingly soluble in hot, very sparingly so in cold water.

The base decolorises potassium permanganate instantly in cold dilute sulphuric acid solution, and gives a Burgundy-red coloration with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate. When dissolved in dilute hydrochloric acid and mixed with sodium nitrite, it yields a colourless, crystalline precipitate, but the product—crystals and mother liquor—when poured into alkaline  $\beta$ -naphthol gives no coloration.

When an aqueous solution of the hydrochloride is mixed with sodium acetate and benzaldehyde, a turbid, yellow solution is produced—evidently owing to the formation of a benzylidene compound.

The composition and mode of formation of the base indicate that it is 2-*p*-bromobenzenehydrazoglyoxaline, or a substance resulting from this by the benzidine or semidine change. The formation of a dihydrochloride and a benzylidene derivative rule out the first suggestion, whilst the formation of the latter compound also eliminates the semidine-type formula III given below. This formula and the benzidine-type formula I are also incompatible with the behaviour of the compound on treatment with nitrous acid and sodium  $\beta$ -naphthoxide, but the semidine-type formula II, representing 2-5'-bromo-2'-aminocanilinoxyoxaline, admits the possibility of *o*-diazimine formation with nitrous acid, and is in harmony with all the observed properties of the compound (compare p. 223).



#### 2-Aminoglyoxaline (XII, p. 223).

For the purification of 2-aminoglyoxaline, crystallisation of the stannichloride and hydrogen oxalate has proved to be useful.

The free base can be obtained (1) from the hydrochloride by the

addition of an equivalent quantity of sodium carbonate, evaporation to dryness, and extraction with alcohol, and (2) from the hydrogen oxalate by treatment with aqueous barium hydroxide, removal of the excess of this by carbon dioxide, and evaporation of the solution under diminished pressure. In either case, it is obtained as a nearly colourless syrup which gradually turns brown on keeping. It is miscible with water and alcohol, sparingly soluble in chloroform, but hardly soluble in ether or benzene.

The *hydrochloride* crystallises from absolute alcohol in long, colourless plates which melt at  $152^{\circ}$  (corr.). It is deliquescent, and readily soluble in cold, very readily so in hot absolute alcohol. Its aqueous solution reacts neutral to litmus.

Found: C=30.2; H=5.2; N=34.7; Cl=29.9.

$C_3H_5N_3.HCl$  (119.5) requires C=30.1; H=5.1; N=35.1; Cl=29.7 per cent.

The *stannichloride* crystallises from two to two and a-half times its weight of 10 per cent. hydrochloric acid in prismatic needles, which are anhydrous and melt at  $286^{\circ}$  (corr.). It is readily soluble in water.

Found: Cl=42.4.

$(C_3H_5N_3)_2.H_2SnCl_6$  (499.6) requires Cl=42.6 per cent.

The *nitrate* separates from water in large, transparent tablets, which are anhydrous, and, after drying at  $100^{\circ}$ , sinter from about  $125^{\circ}$  and melt at  $135$ — $136^{\circ}$  (corr.).

Found: N=38.2.

$C_3H_5N_3.HNO_3$  (146.1) requires N=38.4 per cent.

The *hydrogen oxalate* crystallises from water in large, colourless tablets, which are anhydrous and melt and effervesce at  $211^{\circ}$  (corr.). It is sparingly soluble in cold, readily so in hot water.

Found: N=24.0.

$C_3H_5N_3.C_2H_2O_4$  (173.1) requires N=24.3 per cent.

The *picrate* separates from water in long, glistening, silky needles, or in short, prismatic needles, both melting at  $236^{\circ}$  (corr.) after drying at  $100^{\circ}$ . It is sparingly soluble in cold, fairly readily so in hot water.

*Reactions of 2-Aminoglyoxaline.*—2-Aminoglyoxaline hydrochloride dissolved in dilute aqueous copper sulphate gives on the addition of sodium hydroxide a green precipitate, which rapidly darkens and becomes purple-brown. The same precipitate—evidently a copper salt—is obtained eventually with Fehling's solution; no reduction of this solution takes place even on boiling. 2-Aminoglyoxaline nitrate in aqueous silver nitrate gives a white

precipitate on the addition of ammonia; this precipitate is soluble in excess of ammonia, and the solution deposits metallic silver on heating.

2-Aminoglyoxaline hydrochloride in aqueous solution decolorises aqueous potassium permanganate instantly; with ferric chloride, it gives no coloration. With sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate, it gives a deep red colour. On the addition of sodium nitrite to aqueous 2-aminoglyoxaline hydrochloride, a clear, yellow solution is produced which gives a soluble, brownish cherry-coloured dye with  $\beta$ -naphthol in aqueous sodium hydroxide. An aqueous solution of 2-aminoglyoxaline hydrochloride mixed with dilute aqueous sodium nitroprusside gives, on the addition of sodium hydroxide, a deep blue colour, which slowly changes to a bright chestnut on keeping.

2-Aminoglyoxaline is very stable towards hot acids and alkalis. When boiled with 10 per cent. aqueous sodium hydroxide, no ammonia is evolved, and it can be recovered unchanged from the solution. It can be recovered mainly unchanged after heating with concentrated hydrochloric acid for three hours at  $170^{\circ}$ , and even after three hours at  $200^{\circ}$  a small proportion can be recovered, together with ammonium chloride and other unidentified products.

An aqueous solution of 2-aminoglyoxaline hydrochloride containing an excess of sodium acetate gives no coloration or other evidence of the formation of a benzyldene derivative when mixed with benzaldehyde.

2-Acetylaminoglyoxaline was prepared by boiling 2-aminoglyoxaline hydrochloride with anhydrous sodium acetate and acetic anhydride for one hour, and mixing the product with aqueous sodium carbonate. It crystallises from water in small prisms which melt to a brown liquid at  $287^{\circ}$  (corr.), after sintering and darkening from about  $270^{\circ}$ . It is anhydrous and sparingly soluble in cold water, but fairly readily so in hot water.

Found: C=47.7; H=5.7; N=33.4.

$C_5H_7ON_3$  (125.1) requires C=48.0; H=5.6; N=33.6 per cent.

The reactions of this substance are described with those of the next compound.

2-Benzoylaminoglyoxaline was prepared by the Schotten-Baumann method. The crude product collected from the reaction liquor appears to be a di- or tri-benzoylaminoglyoxaline. After washing with ether to remove benzoic anhydride, it formed a nearly colourless, crystalline powder, which contained only a trace of chloride, but gave an odour of benzoyl chloride when boiled with dilute hydrochloric acid. When treated with a little hot alcohol,



it dissolved, and 2-benzoylaminoglyoxaline crystallised from the hot liquor, whilst the mother liquor from this left an oil—apparently ethyl benzoate—on distillation. 2-Benzoylaminoglyoxaline was purified by crystallisation from alcohol, from which it separates in glistening leaflets, melting at  $227^{\circ}$  (corr.) after sintering earlier. It is sparingly soluble even in hot alcohol, and almost insoluble in boiling water.

Found: C = 63.9; H = 4.9; N = 22.4.

$C_{10}H_9ON_3$  (187.1) requires C = 64.1; H = 4.9; N = 22.5 per cent.

2-Acetylaminoglyoxaline and 2-benzoylaminoglyoxaline are soluble in dilute hydrochloric acid and in aqueous sodium hydroxide, but not in aqueous sodium carbonate. They give cherry-red solutions with sodium diazobenzene-*p*-sulphonate in sodium carbonate, but do not give colorations with sodium nitroprusside and sodium hydroxide. They do not change the colour of cold aqueous acid permanganate, but give green solutions with cold aqueous permanganate in sodium hydroxide solution. When mixed with hydrochloric acid and sodium nitrite, they do not couple with  $\beta$ -naphthol in aqueous sodium hydroxide.

#### *The Benzeneazo-4-methylglyoxalines.*

37.2 Grams of aniline in 100 c.c. of hydrochloric acid and 300 c.c. of water were diazotised with 28.8 grams of sodium nitrite in 150 c.c. of water. The solution was run slowly into a solution of 32.8 grams of 4-methylglyoxaline and 100 grams of sodium hydrogen carbonate in 2 litres of water at  $10^{\circ}$  and kept overnight. The orange precipitate was collected, washed well with water (filtrate *F*), and triturated successively with 500, 250, and 250 c.c. of 2.5 per cent. aqueous hydrochloric acid. The insoluble fraction formed a dark red powder, which amounted to 23.2 grams, and decomposed at  $175^{\circ}$  after sintering from  $160^{\circ}$ . On crystallisation from 300 c.c. of alcohol, it gave 17.3 grams of pure 2:5-bisbenzeneazo-4-methylglyoxaline, the remainder of the material forming a black resin.

The hydrochloric acid extract was basified with sodium carbonate, and gave 40.4 grams of a yellow, crystalline powder, which sintered from  $160^{\circ}$  and decomposed at  $195^{\circ}$ . On crystallisation from 400 c.c. of alcohol, it gave, successively, 13.1 grams melting at  $235^{\circ}$ , 3.9 grams melting at  $232^{\circ}$ , which both gave 5-benzeneazo-4-methylglyoxaline on recrystallisation, then 7.4 grams melting at  $175^{\circ}$ , which gave 2-benzeneazo-4-methylglyoxaline on recrystallisation, then 12.4 grams of a mixture of the two compounds.

Owing to the formation of the bis-compound in the above reaction, the benzenediazonium chloride employed was insufficient to combine with the whole of the methylglyoxaline present, and it was calculated that 10.5 grams of this remained in the filtrate *F*. This was accordingly treated with a diazo-solution prepared from 11.9 grams of aniline, and gave further quantities of the substances described above, 5.3 grams of the bis-compound and 5.6 grams of 5-benzeneazo-4-methylglyoxaline being obtained in a nearly pure state.

*2-Benzeneazo-4-methylglyoxaline* (XIV, p. 224) crystallises from alcohol in orange prisms, which melt at  $185^{\circ}$  (corr.).

Found: C=64.8; H=5.6; N=30.1.

$C_{10}H_{10}N_4$  (185.2) requires C=64.5; H=5.4; N=30.1 per cent.

*5-Benzeneazo-4-methylglyoxaline* (XVIII, p. 224) crystallises from alcohol in flat, glistening, copper-coloured needles, which melt and decompose at  $240^{\circ}$  (corr.).

Found: C=64.5; H=5.6; N=30.0.

$C_{10}H_{10}N_4$  (185.2) requires C=64.5; H=5.4; N=30.1 per cent.

*2:5-Bisbenzeneazo-4-methylglyoxaline* separates from alcohol in prismatic needles and from ethyl acetate in cubes. Both forms are garnet-red in colour and melt and decompose at  $206^{\circ}$  (corr.).

Found: C=66.0, 65.9; H=5.1, 5.1; N=28.8, 28.8.

$C_{16}H_{14}N_6$  (290.2) requires C=66.2; H=4.9; N=29.0 per cent.

This substance is readily soluble in alcohol, ethyl acetate, or acetone, fairly readily so in chloroform, but sparingly so in ether or benzene.

It is soluble in aqueous sodium hydroxide, and is reprecipitated unchanged on the addition of acetic acid. It is only very sparingly soluble in dilute hydrochloric acid. When boiled with 10 per cent. aqueous hydrochloric acid, it is quickly resinified with effervescence, doubtless due to nitrogen, and the production of an odour of phenol.

#### *Reduction of 2-Benzeneazo-4-methylglyoxaline with Stannous Chloride.*

1.5 Grams of 2-benzeneazo-4-methylglyoxaline gave 1.4 grams of 2-amino-5-p-aminophenyl-4-methylglyoxaline dihydrochloride when reduced with stannous chloride in the manner previously described for the lower homologue (p. 238).

*2-Amino-5-p-aminophenyl-4-methylglyoxaline dihydrochloride* crystallises from water in diamond-shaped plates, which are anhydrous and do not melt below  $300^{\circ}$ . It is readily soluble in cold, very readily so in hot water.

Found: C=46.0, 45.9; H=5.5, 5.5.

$C_{10}H_{12}N_4 \cdot 2HCl$  (201.0) requires C=46.0; H=5.4 per cent.

When boiled with an excess of aqueous sodium carbonate and animal charcoal, it yields the *monohydrochloride*, unlike the lower homologue, which yields the corresponding base under this treatment.

The *monohydrochloride* crystallises from alcohol in flat needles which sinter at about 80°, become discoloured rapidly about 240°, and melt at 260° (corr.). It is readily soluble in hot water or alcohol, less so in these solvents when cold.

Found, in air-dried base, loss at 60° in a vacuum, 13.2, 13.3.

$C_{10}H_{12}N_4 \cdot HCl \cdot 2\frac{1}{2}H_2O$  requires loss of  $2H_2O$ =13.4 per cent.

Found, in base so dried: C=51.5; H=5.6; N=24.0, 24.0;  
Cl=14.9.

$C_{10}H_{12}N_4 \cdot HCl \cdot \frac{1}{2}H_2O$  (233.7) requires C=51.4; H=6.0; N=24.0;  
Cl=15.2 per cent.

The *dipicrate* forms glistening, yellow needles, which melt and decompose at 255° (corr.) after darkening earlier. It is very sparingly soluble even in boiling water.

An aqueous solution of the hydrochloride reduces cold ammoniacal silver nitrate. It gives, with Fehling's solution, a greyish-green precipitate, which becomes pale brown on boiling the liquor; with cold aqueous acid permanganate, instant reduction; with sodium diazobenzene-*p*-sulphonate, a pale orange colour, which deepens on keeping; with hydrochloric acid and sodium nitrite, an orange-yellow solution, which yields a sparingly soluble claret dye when added to a solution of  $\beta$ -naphthol in aqueous sodium hydroxide. On the addition of sodium hydroxide to an aqueous solution of the hydrochloride and sodium nitroprusside, an orange colour is produced, which changes to green on the addition of acetic acid.

The *diacetyl* derivative was prepared by the action of sodium acetate and acetic anhydride on the dihydrochloride, and was purified by crystallisation of the hydrochloride.

*2-Acetyl-amino-5-p-acetylaminophenyl-4-methylglyoxaline hydrochloride* crystallises from water in felted, silky needles, which are sparingly soluble in cold water, contain  $4H_2O$ , and, after drying at 100°, melt and decompose at 303° (corr.).

Found, in air-dried salt, loss at 100°=19.0.

$C_{14}H_{16}O_2N_4 \cdot HCl \cdot 4H_2O$  requires  $H_2O$ =18.9 per cent

Found, in salt dried at 100°, Cl=11.4.

$C_{14}H_{16}O_2N_4 \cdot HCl$  (308.7) requires Cl=11.5 per cent.

On adding ammonia to an aqueous solution of the hydrochloride, the base was precipitated in minute, glistening needles, which, after drying at  $100^{\circ}$ , melted to a red liquid at  $280^{\circ}$  (corr.).

*Monobenzylidene Derivative.*—To 0.5 gram of the dihydrochloride in 5 c.c. of water there were added, first, 0.55 gram of sodium acetate in 5 c.c. of water, and then 0.5 c.c. of benzaldehyde, and the mixture was stirred. A yellow colour was developed, and the aqueous liquor became turbid and gradually deposited crystals. On adding a few drops of acetic acid and ether, the quantity of crystals was increased. They were collected and washed with water and ether, when there remained 0.5 gram of a pale yellow, crystalline powder, which proved to be the acetate of 2-amino-5-p-benzylideneaminophenyl-4-methylglyoxaline. When dried at  $100^{\circ}$ , it melts and decomposes at  $208^{\circ}$  (corr.), after sintering and darkening earlier.

Found, in substance dried in a vacuum, C=67.2; H=6.2; N=16.2.\*

$C_{17}H_{16}N_4C_2H_4O_2$  (336.3) requires C=67.8; H=6.0; N=16.7 per cent.

This salt is very sparingly soluble in cold water, but slightly so in boiling water, with which, however, it gives an odour of benzaldehyde, and thus appears to suffer hydrolysis. When mixed with aqueous sodium carbonate, it yields the base as a deep yellow, insoluble gum, which could not be obtained in crystalline form. When the acetate is moistened with 10 per cent. aqueous hydrochloric acid, it turns red, but does not dissolve until the mixture is warmed, when the red colour disappears.

*Reduction of 2-Benzeneazo-4-methylglyoxaline with Zinc Dust and Acetic Acid.*

Two grams of the azo-compound were reduced by the method applied to the lower homologue (p. 241) and worked up in the same manner as far as the removal of the aniline by extraction with ether. The solvent removed 0.65 gram of crude aniline. The alkaline liquor remaining was acidified with hydrochloric acid, evaporated to dryness, and extracted with absolute alcohol, when 1.4 grams of brown syrup were removed. This, when dissolved in a little absolute alcohol and kept, deposited 0.7 gram of nearly pure alacreatinine hydrochloride.

This was converted into the picrate, when a very small quantity of 2-amino-5-p-aminophenyl-4-methylglyoxaline dipicrate separated

\* The substance left a trace of ash on combustion.

from the hot solution, whilst, on cooling, alacreatinine picrate crystallised out. After recrystallisation, the salt was obtained in a pure state, and was converted into the base and hydrochloride by the usual methods.

Alacreatinine crystallises from water in stout, elongated prisms which resemble carbamide, and contain  $1\text{H}_2\text{O}$ , as previously stated by Baumann (*Annalen*, 1873, **167**, 83). After drying at  $100^\circ$ , it melts at  $222\text{--}223^\circ$  (corr.). (Found, in air-dried salt,  $\text{H}_2\text{O}=13.6$ . Calc.:  $13.7$ . Found, in dried salt,  $\text{C}=42.4$ ;  $\text{H}=6.3$ ;  $\text{N}=36.9$ . Calc.:  $\text{C}=42.5$ ;  $\text{H}=6.2$ ;  $\text{N}=37.1$  per cent.)

It does not give Weyl's reaction, and does not reduce cold aqueous acid permanganate, but gives a green solution with cold alkaline permanganate.

The *hydrochloride* crystallises from absolute alcohol in clusters of prisms, which are anhydrous and melt at  $202\text{--}203^\circ$  (corr.). It is very readily soluble in water, sparingly soluble in cold, fairly readily so in hot alcohol.

Found:  $\text{Cl}=23.6$ .

$\text{C}_4\text{H}_7\text{ON}_3\cdot\text{HCl}$  (149.6) requires  $\text{Cl}=23.7$  per cent.

The *picrate* separates from water in yellow, prismatic needles, which are anhydrous and melt and decompose at  $212^\circ$  (corr.) after sintering from about  $200^\circ$ . It is sparingly soluble in cold, fairly readily so in hot water.

Found:  $\text{N}=24.5$ .

$\text{C}_4\text{H}_7\text{ON}_3\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$  (342.2) requires  $\text{N}=24.6$  per cent.

*Reduction of 5-Benzeneazo-4-methylglyoxaline with Stannous Chloride.*

Fourteen grams of the azo-compound were dissolved in a boiling mixture of 70 c.c. of 10 per cent. aqueous hydrochloric acid and 140 c.c. of water, and mixed with 80 c.c. of stannous chloride solution. The crystalline and residual tin salts were separated as in the experiments described earlier, and decomposed separately by hydrogen sulphide. The crystalline salts gave a solution of hydrochlorides, which, when evaporated nearly to dryness and mixed with alcohol, left 6.1 grams of ammonium chloride undissolved. (Alcoholic mother liquor= $A$ .) The residual salts gave a solution of hydrochlorides, which on concentration deposited  $1.7+0.5$  grams of the *hydrochloride*,  $\text{C}_9\text{H}_{10}\text{ON}_2\cdot\text{HCl}$ , described below, and on further concentration and addition of alcohol gave 1.5 grams of ammonium chloride. The alcoholic mother liquor was combined

with *A*, and gave 4.7 grams of aniline, together with 3.8 grams of a brown, gummy, hydrochloride. This was a mixture from which only very small quantities of crystalline compounds were isolated by various methods of treatment.

The *hydrochloride*,  $C_9H_{10}ON_2.HCl$ , crystallises from water in colourless, transparent, rectangular tablets, which melt and effervesce at  $308^\circ$  (corr.) after sintering and darkening earlier. It is readily soluble in hot, less so in cold water, giving a solution which is strongly acid to litmus.

Found, in air-dried salt, loss at  $110^\circ = 1.7$ .

Found, in salt dried at  $110^\circ$ : C=54.8, 54.8, 55.0; H=5.9, 5.0, 5.2; N=13.5; Cl=17.2.

$C_9H_{10}ON_2.HCl$  (198.6) requires C=54.4; H=5.6; N=14.1; Cl=17.8 per cent.

The corresponding *base* is obtained by adding ammonia to a concentrated aqueous solution of the hydrochloride. It crystallises from water in brilliant, elongated prisms, which are anhydrous and melt at  $185^\circ$  (corr.).

Found: C=66.6, 66.1; H=6.2, 6.1; N=17.8, 17.2.

$C_9H_{10}ON_2$  (162.1) requires C=66.6; H=6.2; N=17.3 per cent.

The base is more readily soluble in dilute aqueous sodium hydroxide than in water. With silver nitrate it yields a white precipitate, which dissolves on the addition of ammonia; on boiling this solution, no reduction takes place. The base does not reduce Fehling's solution on boiling.

It is stable towards cold aqueous acid potassium permanganate, but slowly reduces cold alkaline permanganate, giving a green solution. It gives no coloration with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate. When dissolved in hydrochloric acid and mixed with sodium nitrite, it fails to couple with  $\beta$ -naphthol in aqueous sodium hydroxide. The hydrochloride is recovered slightly charred, but otherwise unchanged, after the action of concentrated hydrochloric acid at  $170^\circ$  for two and a-half hours.

The quantity of this compound available was insufficient for the determination of its constitution, and we are consequently unable to offer any suggestion as to how one of the carbon atoms of the starting material has been eliminated. It is perhaps worth recording that the formula  $C_9H_{10}ON_2$  is that of a phenyldihydro-oxalone.

*Reduction of 5-Benzeneazo-4-methylglyoxaline with Zinc Dust and Acetic Acid.*

Ten grams of the azo-compound were dissolved in 150 c.c. of boiling 50 per cent. acetic acid and reduced by adding gradually 16 grams of zinc dust. After removing the zinc as sulphide, the liquor was mixed with 20 c.c. of hydrochloric acid, evaporated to a syrup, and mixed with alcohol, when 1.3 grams of ammonium chloride were collected. The alcoholic mother liquor was deprived of the solvent, dissolved in water, mixed with sodium carbonate, and shaken with ether, when 1.6 grams of the base,  $C_{10}H_{11}ON_3$ , described below, separated as a nearly colourless, insoluble, crystalline powder. The ethereal solution left on evaporation 3.3 grams of aniline. From the alkaline liquor, 5.5 grams of a mauve varnish were obtained, from which only small quantities of crystalline substances could be isolated by various methods of treatment.

The base,  $C_{10}H_{11}ON_3$ , crystallises from water in small, colourless, glistening, rhomboidal plates, which are anhydrous and melt at  $265^\circ$  (corr.). It is very sparingly soluble in cold water, rather more readily in boiling water.

Found: C=63.7; H=6.2; N=22.0.

$C_{10}H_{11}ON_3$  (189.2) requires C=63.5; H=5.9; N=22.2 per cent.

The *hydrochloride* crystallises from absolute alcohol in transparent, oblong plates which melt at  $206-208^\circ$  (corr.). It is readily soluble in water, concentrated hydrochloric acid, or hot alcohol. Its aqueous solution reacts strongly acid to litmus.

The base dissolves slowly in cold 10 per cent. aqueous sodium hydroxide, readily on warming, and a well-crystallised sodium salt separates from the solution in prismatic needles. This salt is decomposed by carbon dioxide with the regeneration of the base. A solution of the base in aqueous sodium hydroxide gives with Fehling's solution no change in the cold, but a green precipitate on boiling. A solution of the base in nitric acid gives no precipitate with silver nitrate, but on the addition of ammonia a white precipitate, which dissolves on heating the solution, reappears on cooling, and is soluble in excess of ammonia. An aqueous solution of potassium permanganate is unaffected by a solution of the base in sulphuric acid, but turns green with a solution of the base in aqueous sodium hydroxide. The base does not couple with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate, and when dissolved in hydrochloric acid and mixed with sodium nitrite does not couple with sodium  $\beta$ -naphthoxide.

When the hydrochloride is heated with concentrated hydrochloric

sodium nitrite a deep orange solution, which yields a sparingly soluble purple dye with sodium  $\beta$ -naphthoxide. On mixing a solution of the hydrochloride in dilute acetic acid with sodium acetate and benzaldehyde, there is evidence of the formation of a benzylidene derivative. When an aqueous solution of the hydrochloride is mixed with sodium nitroprusside, a pale buff precipitate is formed, which dissolves in sodium hydroxide, giving a deep red solution.

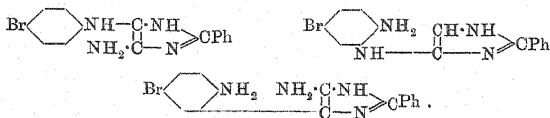
The *triacetyl* derivative was obtained by heating the hydrochloride for one hour on the water-bath with an excess of acetic anhydride and anhydrous sodium acetate. On heating the product with aqueous sodium carbonate, it separated as a slate-grey, crystalline powder, which did not melt at  $300^{\circ}$ .

Found: C=55.2; H=4.1; N=12.6, 12.7; Br=17.3.

$C_{21}H_{19}O_3N_4Br$  (455.2) requires C=55.4; H=4.2; N=12.3;  
Br=17.6 per cent.

It is almost insoluble in boiling water or alcohol, and does not dissolve in dilute acids or in aqueous sodium hydroxide.

From its mode of formation, composition, and properties, it is clear that the hydrochloride,  $C_{15}H_{13}N_4Br \cdot 2HCl$ , arises from 2-phenyl-4-*p*-bromobenzenehydrazoglyoxaline by a change of the semidine or benzidine type, but it is not possible to decide definitely without further evidence which of the three formulæ given below represents its constitution.



*2-p-Sulphobenzenediazoglyoxaline-4:5-dicarboxylic Acid*  
(XX, p. 226).

20.8 Grams of sulphanilic acid were converted into diazobenzene-*p*-sulphonic acid, and the moist crystals (representing about 20 grams of dry substance) were added to a cold solution of 16 grams of glyoxaline-4:5-dicarboxylic acid in 240 c.c. of 10 per cent. aqueous sodium hydroxide. After keeping for one and a-half hours, the liquor was mixed with sufficient glacial acetic acid (36 c.c.) to neutralise the alkali, cooled, and kept for half an hour, when a mass of silky, yellow needles—the disodium salt of the new



acid, separated. These were recrystallised twice from 200 c.c. of water, and finally dissolved in 150 c.c. of hot water and mixed with 50 c.c. of hydrochloric acid, when 12 grams of 2-*p*-sulphobenzeneazoglyoxaline-4:5-dicarboxylic acid separated in red, microscopic prisms mixed with some smaller crystals of glyoxaline-4:5-dicarboxylic acid, from which it was purified by fractional crystallisation from water.

The acid separates from water with  $2\text{H}_2\text{O}$ , which is lost at  $130^\circ$  in a vacuum, but not at  $100\text{--}110^\circ$  under normal pressure.

Found, in air-dried substance, loss at  $130^\circ$  in a vacuum = 10.0;

C = 35.5; H = 3.3; N = 15.1; S = 8.2.

$\text{C}_{11}\text{H}_8\text{O}_7\text{N}_4\text{S}\cdot 2\text{H}_2\text{O}$  (376.2) requires  $\text{H}_2\text{O}$  = 9.6; C = 35.1; H = 3.3; N = 14.9; S = 8.5 per cent.

It is sparingly soluble in cold water, but readily so in hot. It is soluble in aqueous alkalis, but not more soluble in dilute aqueous mineral acids than in water.

The disodium salt separates in yellow, silky needles, which contain  $3\text{H}_2\text{O}$ , when the acid is dissolved in aqueous sodium hydroxide and sufficient acetic acid is added to combine with the alkali. It is readily soluble in hot water, somewhat sparingly so in cold.

Found, in air-dried salt, loss at  $100^\circ$  = 11.6, 12.6.

$\text{C}_{11}\text{H}_6\text{O}_7\text{N}_4\text{SNa}_2\cdot 3\text{H}_2\text{O}$  (438.2) requires  $3\text{H}_2\text{O}$  = 12.3 per cent.

Found, in salt dried at  $100^\circ$ , S = 8.2; N = 11.7.

$\text{C}_{11}\text{H}_6\text{O}_7\text{N}_4\text{SNa}_2$  (384.2) requires S = 8.4; N = 12.0 per cent.

*Reduction of 2-p-Sulphobenzeneazoglyoxaline-4:5-dicarboxylic Acid: Formation of 2-Aminoglyoxaline-4:5-dicarboxylic Acid (XXI, p. 226).*

6.2 Grams of the disodium salt were dissolved in 60 c.c. of 10 per cent. aqueous sodium hydroxide, mixed with 12 grams of sodium hyposulphite (80 per cent.), and boiled. The nearly colourless solution was kept overnight, acidified with hydrochloric acid, boiled, and filtered hot, when 1.6 grams of crude 2-aminoglyoxaline-4:5-dicarboxylic acid separated. This was purified by solution in aqueous sodium hydroxide, filtration, and reprecipitation with hydrochloric acid, and finally crystallised from about 500 c.c. of dilute hydrochloric acid.

2-Aminoglyoxaline-4:5-dicarboxylic acid forms minute, pale buff needles, which effervesce at  $245^\circ$  (corr.) and then melt. It is very sparingly soluble in cold water, a little more readily in hot.

Found, in substance dried at  $110^{\circ}$ ,  $C=34.6$ ;  $H=3.2$ ;  $N=24.6$ .  $C_5H_5O_4N_3$  (171.1) requires  $C=35.1$ ;  $H=3.0$ ;  $N=24.6$  per cent.

It is soluble in aqueous alkalis, but not appreciably more soluble in dilute acids than in water. An aqueous solution, acidified with sulphuric acid, decolorises cold aqueous permanganate instantly. When treated with hydrochloric acid and sodium nitrite and poured into a solution of  $\beta$ -naphthol in aqueous sodium hydroxide, it gives a reddish-brown colour. With sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate, it gives a reddish-brown colour. It does not give any characteristic colour with sodium nitroprusside and sodium hydroxide.

*Action of Water at  $170^{\circ}$ .*—After a preliminary experiment, in which it was found that the product contained ammonium carbonate, 1.33 grams of the acid and 30 c.c. of water were heated in a sealed tube for twelve hours at  $170^{\circ}$ , when a dark brown deposit formed. After adding alkali and distilling into standard acid, 0.157 gram of ammonia was found, whereas 0.132 gram represents the liberation of one molecular proportion. From the residue of the distillation, small quantities of a crystalline picrate were isolated, but in insufficient amount for characterisation.

*Action of Boiling Aniline.*—0.9 Gram of the acid was boiled with 10 c.c. of aniline for six hours under a reflux condenser, in which a small quantity of ammonium carbonate collected. The product was distilled with steam to remove aniline, and left a pale brown, aqueous liquor containing some resinous matter. The liquor was cooled, filtered, and mixed with cold saturated aqueous picric acid, when 1.0 gram of a crystalline picrate, melting at about  $215^{\circ}$ , was obtained. After crystallising this from water twice, it gave 0.4 gram of 2-aminoglyoxaline picrate, melting at  $234^{\circ}$  (corr.), the pure substance melting at  $236^{\circ}$ , and a mixture of the two at  $234^{\circ}$  in the same bath. From the picrate, the hydrochloride and stannichloride were prepared, and identified as the salts of 2-aminoglyoxaline previously described.

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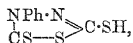
[Received, February 7th, 1919.]

XXVII.—*Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. Part IV. Chain Compounds of Sulphur* (continued).

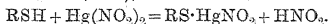
By PRAFULLA CHANDRA RÂY and PRAFULLA CHANDRA GUHA.

IN this investigation, the reactions of several actual and potential mercaptans, some of them cyclic, have been studied. It was expected that in these, the molecules being of a more complex nature, the radicle, especially  $\cdot\text{SHgNO}_2$ , would far more readily part company with the parent substance and lead an independent existence as the compound,  $3(\text{SHgNO}_2)\cdot\text{HgO}$  (T., 1917, 111, 101). The result has proved to be just the reverse.

5-Thiol-2-thio-3-phenyl-2:3-dihydro-1:3:4-thiodiazole,

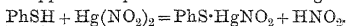


yields, with mercuric nitrite, the corresponding mercaptide nitrite (compare T., 1916, 109, 131),

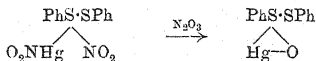


Mercuric nitrite and phenyl mercaptan furnish a compound,  $\text{Ph}_2\text{S}_2\text{Hg}$ , evidently a mercaptide, and sometimes another oxy-salt,  $(3\text{PhS}\cdot\text{HgO})_2$ . It is only in exceptional cases (see p. 264) that the expected mercaptide nitrite,  $\text{PhS}\cdot\text{HgNO}_2$ , is obtained, and then only in an impure form.

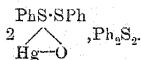
The reaction appears to proceed in the following stages:



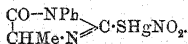
The nitrous acid thus liberated oxidises another pair of molecules of phenyl mercaptan to diphenyl disulphide, and the latter then forms with mercuric nitrite the compound,



Two molecules of this compound combine with a molecule of diphenyl disulphide, giving rise to the compound,

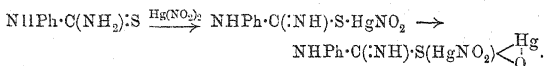


3-Phenyl-5-methyl-2-thiohydantoin gives the mercaptide nitrite,

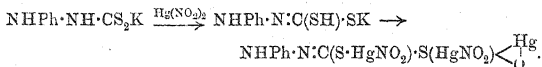


*Potential Mercaptans.*

The interaction of mercuric nitrite and the aryl substituted thiocarbamides, thiosemicarbazides, thiocarbazides, etc., follows the ordinary course, but no detachment of the organic radicle takes place. Thus with phenylthiocarbamide we have



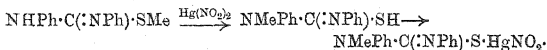
Attention may also here be directed to the interesting analogous case of potassium phenyldithiocarbazine, which combines in itself the function of a real and of a potential mercaptan, thus:



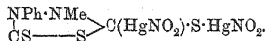
The sulphur atom belonging to the potential mercaptan alone becomes quadrivalent.

*Migration of Alkyl Radicles.*

When thiocarbamilide methyl ether is treated with mercuric nitrite, the methyl group migrates to the neighbouring nitrogen atom, hydrogen taking its place, thus:



That the reactions described above are of wide application is borne out by the behaviour of 5-methylthiol-2-thio-3-phenyl-2:3-dihydro-1:3:4-thiodiazole, which with mercuric nitrite gives the compound,

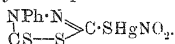
*Reaction with the Alkyl Iodides: Formation of Mono, Di, and Tri-sulphonium Compounds.*

The reaction follows the general course with this material difference, that the complex radicle, being overweighted, can no longer retain its entity, but the less stable part of it is usually ruptured. Of special significance from this point of view is the rupture of the ring of the heterocyclic mercaptide nitrites. When the mercaptide nitrite of 5-thiol-2-thio-3-phenyl-2:3-dihydro-1:3:4-



## EXPERIMENTAL.

*Interaction of the Potassium Salt of 5-Thiol-2-thio-3-phenyl-2:3-dihydro-1:3:4-thiodiazole and Mercuric Nitrite: Formation of the corresponding Mercaptide Nitrite,*



The mercury salt was obtained sometimes anhydrous, but often combined with three, five, or eight molecules of water, the degree of hydration evidently depending on the dilution of the reacting substances. They all evolved nitrous fumes when treated with hydrochloric acid:

0.2724 gave 0.1187 Hg. Hg=43.59.

0.1100 „ 0.0810 CO<sub>2</sub> and 0.0187 H<sub>2</sub>O. C=20.08; H=1.89.

0.1420 „ 10.2 c.c. N<sub>2</sub> at 25° and 760 mm. N=8.10.

C<sub>8</sub>H<sub>5</sub>O<sub>2</sub>N<sub>3</sub>S<sub>3</sub>Hg requires Hg=42.46; C=20.38; H=1.06; N=8.92 per cent.

The above with 3H<sub>2</sub>O:

Found: Hg=38.05; C=18.28; H=3.29; N=8.30; S=18.56.

Calc.: Hg=38.09; C=18.29; H=2.1; N=8.00; S=18.29 per cent.

The compound with 5H<sub>2</sub>O:

Found: Hg=35.75; C=16.92; H=3.20.

Calc.: Hg=35.65; C=17.12; H=2.67 per cent.

The compound with 8H<sub>2</sub>O:

Found: Hg=32.10; C=15.10; H=3.56; N=6.16; S=15.08.

Calc.: Hg=32.52; C=15.63; H=3.41; N=6.83; S=15.61 per cent.

*Mercuric Nitrite and Phenyl Mercaptan.*

Three different compounds have been isolated in this case. When an alcoholic solution of phenyl mercaptan is added slowly to an excess of mercuric nitrite solution, the reaction takes the ordinary course, and the mercaptide nitrite, PhS·HgNO<sub>2</sub>, is mainly formed. It is a dull yellow, light granular powder, and is a true nitrite. When, however, the mercaptan is rapidly added in excess, the whole of the mixture assumes a dirty yellow colour and nitrous fumes are evolved. On keeping, a white, granular powder is obtained which, when crystallised from hot benzene until quite pure, melts sharply at 146°. Under slightly varying conditions, an oxy-compound, (3PhS·HgO)<sub>2</sub>, is formed. As is evident, it is not easy to control the reaction so as to give one product to the ex-

clusion of the others. The mercaptide nitrite is always found to be admixed with the other products of this reaction.

The mercaptide nitrite gave different results of analysis on different occasions, depending on the proportion of the compound,  $\text{Ph}_2\text{S}_3\text{Hg}$ , admixed with it; generally, however, the values were found to be intermediate between those required for the pure material and the compound,  $\text{Ph}_2\text{S}_3\text{Hg}$ .

The compound,  $\text{Ph}_3\text{S}_3\text{Hg}$ , melting at  $146^\circ$ , gave the following results:

0.1942 gave 0.0864 Hg and 0.3134  $\text{BaSO}_4$ . Hg=44.48; S=22.16.

0.0964 gave 0.116  $\text{CO}_2$  and 0.0230  $\text{H}_2\text{O}$ . C=32.17; H=2.7.

$\text{C}_{12}\text{H}_{10}\text{S}_3\text{Hg}$  requires Hg=44.44; S=21.30; C=32.00; H=2.30 per cent.

The compound,  $(3\text{PhS},\text{HgO})_2$ , gave the following results:

0.4016 gave 0.1506 Hg. Hg=37.50.

0.4333 „ 0.5620  $\text{BaSO}_4$ . S=17.82.

0.1230 „ 0.1886  $\text{CO}_2$ . C=41.81.

$\text{C}_{36}\text{H}_{30}\text{O}_2\text{S}_6\text{Hg}_2$  requires Hg=38.02; S=18.25; C=41.07 per cent.

The above two compounds were proved to be non-nitrogenous by combustion analysis.

#### *Mercuric Nitrite and 3-Phenyl-5-methyl-2-thiohydantoin:*

Formation of the Compound,  $\begin{array}{c} \text{CO-NPh} \\ | \\ \text{CHMe}\cdot\text{N} \end{array} \text{S} \cdot \text{HgNO}_2, 2\text{H}_2\text{O}$ .

The compound was greenish-grey:

0.1981 gave 0.0954  $\text{HgS}$  and 0.1110  $\text{BaSO}_4$ . Hg=41.51; S=7.69.

0.1774 gave 0.1586  $\text{CO}_2$  and 0.0582  $\text{H}_2\text{O}$ . C=24.38; H=3.65.

0.2836 „ 20.8 c.c.  $\text{N}_2$  at  $30^\circ$  and 760 mm. N=8.10.

$\text{C}_{10}\text{H}_{13}\text{O}_5\text{N}_3\text{SHg}$  requires Hg=41.07; S=6.57; C=24.64; H=2.67; N=8.63 per cent.

#### *Potential Mercaptans.*

*Mercuric Nitrite and Phenylthiocarbamide: Formation of the*

*Compound,  $\text{NHPh}\cdot\text{C}(\text{:NH})\cdot\text{S}(\text{HgNO}_2)\begin{array}{c} \text{Hg} \\ | \\ \text{O} \end{array}$ .*

This was deep yellow:

0.3512 gave 0.2350 Hg and 0.1227  $\text{BaSO}_4$ . Hg=66.9; S=4.8.

0.2015 „ 11.4 c.c.  $\text{N}_2$  at  $26^\circ$  and 760 mm. N=6.40.

$\text{C}_7\text{H}_7\text{O}_3\text{N}_3\text{SHg}_2$  requires Hg=65.25; S=5.22; N=6.85 per cent.

*Mercuric Nitrite and s-Diphenylthiocarbamide: Formation of the Compound,  $\text{NHPh}\cdot\text{C}(\text{:NPh})\cdot\text{S}(\text{HgNO}_2)\text{O}^{\text{Hg}}$ .*

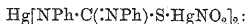
This was a brownish-yellow, granular powder:

0.3422 gave 0.1970 Hg and 0.1069  $\text{BaSO}_4$ . Hg=57.57; S=4.64.

0.3970 „ 0.1141  $\text{CO}_2$  and 0.0244  $\text{H}_2\text{O}$ . C=22.27; H=1.94.

$\text{C}_{13}\text{H}_{11}\text{O}_3\text{N}_3\text{SHg}_2$  requires Hg=58.07; S=4.64; C=22.64; H=1.60 per cent.

The above compound is only rarely formed. The product generally obtained conforms to the formula



0.1555 gave 0.0947 HgS and 0.0741  $\text{BaSO}_4$ . Hg=52.51; S=6.55.

0.2275 gave 0.1367 HgS and 0.0992  $\text{BaSO}_4$ . Hg=51.80; S=5.99.

$\text{C}_{26}\text{H}_{20}\text{O}_4\text{N}_6\text{S}_2\text{Hg}_3$  requires Hg=52.43; S=5.59 per cent.

*Mercuric Nitrite and Thiosemicarbazide: Formation of the Compound,  $\text{Hg}[\text{N}(\text{NH}_2)\cdot\text{C}(\text{:NH})\cdot\text{S}\cdot\text{HgNO}_2]_2$ .*

An aqueous solution of the thio-compound was used. The product was a dull yellow, granular powder:

0.2715 gave 0.1870 HgS and 0.1362  $\text{BaSO}_4$ . Hg=68.87; S=6.89.

0.1032 gave 11.8 c.c.  $\text{N}_2$  at  $32^\circ$  and 760 mm. N=12.60.

$\text{C}_2\text{H}_6\text{O}_4\text{N}_8\text{S}_2\text{Hg}_3$  requires Hg=68.96; S=7.36; N=12.87 per cent.

*Mercuric Nitrite and Diphenylthiosemicarbazide: Formation of the Compound,  $\text{Hg}[\text{N}(\text{NHPh})\cdot\text{C}(\text{:NPh})\cdot\text{S}\cdot\text{HgNO}_2]_2$ .*

This is an orange-yellow, granular powder:

0.1797 gave 0.0925 Hg. Hg=51.48.

0.2577 „ 0.2498  $\text{CO}_2$  and 0.0523  $\text{H}_2\text{O}$ . C=26.21; H=2.25.

0.1380 „ 11.7 c.c.  $\text{N}_2$  at  $32^\circ$  and 760 mm. N=9.38.

$\text{C}_{26}\text{H}_{22}\text{O}_4\text{N}_8\text{S}_2\text{Hg}_3$  requires Hg=51.11; C=28.57; H=1.87; N=9.54 per cent.



*Mercuric Nitrite and Diphenylthiocarbazide: Formation of the Compound,  $\text{Hg}[\text{N}(\text{NHPh}) \cdot \text{C}(\cdot\text{N} \cdot \text{NHPh}) \cdot \text{S} \cdot \text{HgNO}_2]_2$ .*

This is a pink, granular powder:

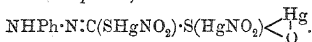
0.1667 gave 0.0965 HgS and 0.0607 BaSO<sub>4</sub>. Hg=49.91;  
S=5.00.

0.1463 gave 0.1404  $\text{CO}_2$  and 0.0327  $\text{H}_2\text{O}$ . C=26.14; H=2.48.

0.1167    „    11.7 c.c. N<sub>2</sub> at 30° and 760 mm. N=11.26.

$C_{26}H_{24}O_4N_{10}S_2Hg_3$  requires Hg=49.83; S=5.31; C=25.91;  
H=1.82; N=11.62 per cent.

*Mercuric Nitrite and Phenylhydrazine Phenyldithiocarbazinate:  
Formation of the Compound.*



This is a blackish-violet, granular powder:

0.1971 gave 0.1549 HgS and 0.1031 BaSO<sub>4</sub>. Hg=67.71;  
S=7.18.

0.1651 gave 8.5 c.c.  $N_2$  at  $27^\circ$  and 760 mm.  $N=5.89$ .

$C_7H_6O_5N_4S_2Hg_8$  requires Hg=67.40; S=7.19; N=6.30; C=9.44  
per cent.

The same compound is formed by the interaction of mercuric nitrite and potassium phenyldithiocarbazinate. (Found: Hg=67.97; C=9.24; H=0.98; N=5.88 per cent.)

*Mercuric Nitrite and Thiocarbonyl Methyl Ether: Formation of the Compound,  $\text{NMePh}\cdot\text{C}(\text{NPh})\cdot\text{S}\cdot\text{HgNO}_2$ .*

This is an orange-yellow, granular powder:

0.2801 gave 0.1038 Hg. Hg=39.86.

0.2377, 0.3027 CO<sub>2</sub> and 0.0738 H<sub>2</sub>O. C=34.70; H=3.45.

0.2863    "    22.6 c.c. N<sub>2</sub> at 29° and 760 mm.    N=8.99.

$C_{14}H_{13}O_2N_3SHg$  requires Hg=40.90; C=34.50; H=2.67;  
N=8.86 per cent.

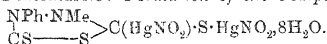
*Mercuric Nitrite and Thiocarbamylide Ethyl Ether: Formation of the Compound,  $\text{NEtPh}\cdot\text{C}(\text{NPh})\cdot\text{S}\cdot\text{HgNO}_2$ .*

The substance is an orange-yellow, granular powder:

0.3730 gave 0.1478 Hg and 0.1874 BaSO<sub>4</sub>. Hg=39.63; S=6.91.

0.1232 „ 9.4 c.c. N<sub>2</sub> at 32° and 760 mm. N=8.43.

$C_{15}H_{15}O_3N_3SHg$  requires Hg=39.92; S=6.39; N=8.38 per cent.

*Mercuric Nitrite and 5-Methylthiol-2-thio-3-phenyl-2:3-dihydro-1:3:4-thiodiazole: Formation of the Compound,*

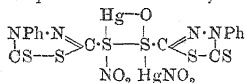
A clear solution of the thio-compound in chloroform was vigorously agitated with mercuric nitrite solution for nearly half an hour, when an emulsion was formed which, after being allowed to remain overnight, gave a cream-coloured, granular mass:

0.1984 gave 0.1055 HgS and 0.1384 BaSO<sub>4</sub>. Hg=45.85.  
S=9.58.

0.1879 gave 0.0884 CO<sub>2</sub> and 0.0296 H<sub>2</sub>O. C=12.83; H=1.75.

0.1603 ,, 10.2 c.c. N<sub>2</sub> at 30° and 760 mm. N=7.03.

C<sub>9</sub>H<sub>24</sub>O<sub>12</sub>N<sub>4</sub>S<sub>3</sub>Hg<sub>2</sub> requires Hg=45.67; S=10.96; C=12.33;  
H=0.91; N=6.39 per cent.

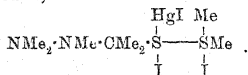
*Mercuric Nitrite and 2-Thio-3-phenyl-2:3-dihydro-1:3:4-thiodiazole Disulphide: Formation of the Compound,*

(compare T., 1916, 109, 133):

0.2940 gave 0.1288 Hg. Hg=43.80.

0.1190 ,, 9.00 c.c. N<sub>2</sub> at 30° and 760 mm. N=8.35.

C<sub>16</sub>H<sub>10</sub>O<sub>5</sub>N<sub>6</sub>S<sub>6</sub>Hg<sub>2</sub> requires Hg=41.75; N=8.77 per cent.

*Reaction with the Alkyl Iodides.**Interaction of the Mercaptide Nitrite of 5-Thiol-2-thio-3-phenyl-2:3-dihydro-1:3:4-thiodiazole and Methyl Iodide: Formation of the Compound,*

The method of procedure is exactly the same as in the interaction of simple mercury mercaptide nitrites and the alkyl iodides. After heating with methyl iodide under reflux, a portion was left undissolved, which, when purified by washing several times with acetone, melted sharply at 127°. The portion soluble in acetone was purified by precipitation with ether, and melted at 107°:

0.3129 gave 0.0811 Hg. Hg=25.92.

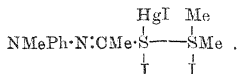
0.4107 „ 0.1066 Hg and 0.3718 AgI. Hg=25.96; I=48.72.

0.0844 „ 0.0363 CO<sub>2</sub> and 0.0237 H<sub>2</sub>O. C=11.73; H=2.45.

C<sub>8</sub>H<sub>21</sub>N<sub>2</sub>I<sub>3</sub>S<sub>2</sub>Hg requires Hg=25.32; I=48.23; C=12.15;

H=2.66 per cent.

The compound insoluble in acetone has the formula



0.1867 gave 0.0449 Hg, 0.1527 AgI, and 0.0870 BaSO<sub>4</sub>.  
Hg=25.96; I=48.93; S=6.40.

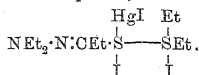
0.1070 gave 0.0590 CO<sub>2</sub> and 0.0734 H<sub>2</sub>O. C=15.06; H=1.39.

0.1227 „ 4.2 c.c. N<sub>2</sub> at 35° and 760 mm. N=3.7.

C<sub>11</sub>H<sub>17</sub>N<sub>2</sub>I<sub>3</sub>S<sub>2</sub>Hg requires Hg=24.33; I=46.35; S=7.79;

C=16.06; H=2.87; N=3.4 per cent.

*Interaction of the above Mercaptide Nitrite and Ethyl Iodide:  
Formation of the Compound,*



(m. p. 73–74°).

0.2316 gave 0.0572 Hg, 0.1960 AgI, and 0.0972 BaSO<sub>4</sub>.  
Hg=24.69; I=45.74; S=5.77.\*

0.2564 gave 0.0611 Hg. Hg=23.83.

0.1278 „ 0.0703 CO<sub>2</sub> and 0.0296 H<sub>2</sub>O. C=15.41; H=2.58.

0.2470 „ 7.8 c.c. N<sub>2</sub> at 31° and 760 mm. N=3.50.

C<sub>11</sub>H<sub>25</sub>N<sub>2</sub>I<sub>3</sub>S<sub>2</sub>Hg requires Hg=24.09; I=45.90; S=7.72; C=15.90;  
H=3.07; N=3.57 per cent.

*Phenyl Mercaptide Nitrite and Methyl Iodide: Formation of the  
Compound, PhMeS<sub>2</sub>HgI<sub>2</sub>MeI.*

The pure substance was obtained by repeated crystallisation, and was a dull yellow, crystalline powder melting at 90°:

0.4616 gave 0.1252 Hg and 0.4353 AgI. Hg=27.12; I=50.96.

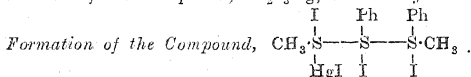
0.1131 „ 0.0551 CO<sub>2</sub>. C=13.29.

C<sub>8</sub>H<sub>11</sub>I<sub>3</sub>S<sub>2</sub>Hg requires Hg=26.6; I=50.66; C=12.77 per cent.

\* See footnote, p. 271.

*Phenyl Mercaptide Nitrite and Ethyl Iodide: Formation of the Compound, PhEtS<sub>2</sub>HgI<sub>2</sub>, EtI (m. p. 59°).*

0.2994 gave 0.0774 Hg and 0.2673 AgI. Hg=25.85; I=48.24.  
 0.1302 ,, 0.0740 CO<sub>2</sub> and 0.0282 H<sub>2</sub>O. C=15.5; H=1.86.  
 C<sub>10</sub>H<sub>15</sub>I<sub>3</sub>S<sub>2</sub>Hg requires Hg=25.64; I=48.84; C=15.39; H=1.92  
 per cent.

*Interaction of the Compound, Ph<sub>2</sub>S<sub>2</sub>Hg, and Methyl Iodide:*

The product was an oil which, on stirring, crystallised. It was washed several times with acetone, when the colour changed to yellowish-white. It was insoluble in acetone, and melted at 111—112°:

0.3150 gave 0.0615 Hg, 0.2915 AgI, and 0.2007 BaSO<sub>4</sub>.  
 Hg=19.53; I=50.00; S=8.75.  
 0.1410 gave 0.0902 CO<sub>2</sub> and 0.0390 H<sub>2</sub>O. C=17.41; H=3.07.  
 C<sub>14</sub>H<sub>16</sub>I<sub>4</sub>S<sub>3</sub>Hg requires Hg=20.24; I=51.42; S=9.71; C=17.00;  
 H=1.62 per cent.

It will be noticed that whenever a sulphonium compound contains phenyl groups, it becomes insoluble in acetone.

*Mercaptide Nitrite of Thiocarbanilide and Ethyl Iodide:**Formation of the Compound, CEt<sub>2</sub>ISEtI·HgI.*

In this case, deep purple, needle-shaped crystals were obtained which were soluble in acetone:

0.3083 gave 0.0890 Hg, 0.2920 AgI, and 0.1042 BaSO<sub>4</sub>.  
 Hg=28.73; I=51.18; S=4.64.  
 0.1214 gave 0.0552 CO<sub>2</sub> and 0.0232 H<sub>2</sub>O. C=12.04; H=2.12.  
 C<sub>7</sub>H<sub>15</sub>I<sub>3</sub>SHg requires Hg=28.09; I=53.51; S=4.49; C=11.80;  
 H=2.11 per cent.

*Mercaptide Nitrite of Thiocarbanilide Methyl Ether and Methyl Iodide: Formation of the Compound, Me<sub>2</sub>S<sub>2</sub>HgI<sub>2</sub>, MeI.*

The mercaptide nitrite was heated under reflux with methyl iodide. It was obtained pure by fractional precipitation from a

concentrated solution in acetone by adding ether and repeating the process five or six times, when a fairly good crop was obtained which melted at 160—162°:

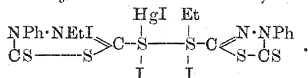
0.3290 gave 0.0791 Hg and 0.3281 AgI. Hg=29.51; I=53.89.  
 0.1150 „ 0.0221 CO<sub>2</sub> and 0.0218 H<sub>2</sub>O. C=5.24; H=2.11.  
 C<sub>3</sub>H<sub>9</sub>I<sub>3</sub>S<sub>2</sub>Hg requires Hg=28.98; I=55.21; C=5.22; H=1.30  
 per cent.

*Mercaptide Nitrite of Thiocarbanilide Ethyl Ether and Ethyl Iodide: Formation of the Compound, Et<sub>2</sub>S<sub>2</sub>HgI<sub>2</sub>, EtI.*

The procedure was almost the same as in the previous instance. On concentrating the acetone solution, a portion crystallised out, which was purified by repeated fractional crystallisation; when pure, it melted sharply at 111°:

0.3127 gave 0.0862 Hg and 0.0978 AgI. Hg=27.57; I=51.46.  
 0.0861 „ 0.0327 CO<sub>2</sub> and 0.0255 H<sub>2</sub>O. C=10.37; H=3.29.  
 C<sub>6</sub>H<sub>15</sub>I<sub>3</sub>S<sub>2</sub>Hg requires Hg=27.32; I=52.05; C=10.37; H=3.29  
 per cent.

*2-Thio-3-phenyl-2:3-dihydro-1:3:4-thiodiazole Disulphide, Mercuric Iodide, and Ethyl Iodide: Formation of the Compound,*



0.3127 gave 0.0512 Hg, 0.2366 AgI, and 0.3026 BaSO<sub>4</sub>.  
 Hg=16.38; I=40.89; S=13.29.\*  
 0.1574 gave 0.1066 CO<sub>2</sub>. C=18.47.  
 C<sub>20</sub>H<sub>20</sub>N<sub>4</sub>I<sub>4</sub>S<sub>6</sub>Hg requires Hg=16.45; I=41.75; S=15.75; C=19.74  
 per cent.

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\* Owing to the tedious process involved in analysis, the values for sulphur and iodine are sometimes too low (compare T., 1916, 109, 135).

## XXVIII.—*The Reaction between Sodium Chloride Solution and Metallic Magnesium.*

By WILLIAM HUGHES.

Cold aqueous solutions of various salts, including sodium chloride, sodium hydrogen carbonate, sodium carbonate, and magnesium sulphate, were found to react with magnesium powder with considerably more speed than one would expect, since cold water acts very slowly on the metal, and solutions of alkali hydroxides not at all.

That the metal slowly dissolves in solutions of its own salts with the formation of hydrogen, the hydroxide, or a basic salt, has been observed by Kippenberger (*Chem. Zeit.*, 1895, **19**, 269), Vitali (*L'Orosi*, 1895, **18**, 289), Lemoine (*Compt. rend.*, 1899, **129**, 291), Bryant (*Chem. News*, 1899, **79**, 75), Kahlenberg (*J. Amer. Chem. Soc.*, 1903, **25**, 380), and Roberts and Brown (*ibid.*, 1903, **25**, 801).

Liberation of the metal together with hydrogen from various salt solutions by magnesium has been described by Commaille (*Compt. rend.*, 1866, **63**, 556), Clowes and Caven (P., 1897, **13**, 221), Divers (P., 1898, **14**, 57), Tommasi (*Bull. Soc. chim.*, 1899, [iii], **21**, 885), and Faktor (*Pharm. Post*, 1905, **38**, 153).

Lohnstein (*Zeitsch. Elektrochem.*, 1907, **13**, 612) found that the action of magnesium on acetic acid was catalysed positively by the addition of some salts and negatively by others.

Knapp (*Chem. News*, 1912, **105**, 253) found that palladium chloride solutions, and Michailenko and Mushinsky (*J. Russ. Phys. Chem. Soc.*, 1912; **44**, 181) that the water of crystallisation of certain salts, were acted on by magnesium with the evolution of hydrogen.

### EXPERIMENTAL.

In the preliminary experiments, it was found that 0.329 gram of ordinary magnesium powder and 35.3 c.c. of 2*N*-sodium chloride solution gave 291.4 c.c. of a gas at the end of a week. The metal darkened, and a white, gelatinous solid was disseminated throughout the liquid. The greyish-black powder slowly changed to a compact, white solid, but the reaction was not quite complete at the end of seven days. The theoretical yield of hydrogen is 325 c.c. at *N.T.P.*

One c.c. of the original sodium chloride solution and 1 c.c. of the solution which had been acted on by the magnesium gave a

titre of 13.62 c.c. and 13.70 c.c. respectively with silver nitrate. 38.6 C.c. of the gas after absorption for fifteen minutes over freshly prepared alkaline pyrogallol measured 37.5 c.c.

These results were taken to indicate that the gas was hydrogen only, and it was determined to seek a relation, if any, between the rate of evolution of gas and the concentration of the sodium chloride solution.

The method adopted was to add known amounts of magnesium to the different solutions which had been saturated with hydrogen, and to measure the initial velocity of the reaction by reading the volume of hydrogen evolved at 25°, without shaking, at short intervals for a total period of two or three minutes.

*Magnesium.*—A supply of ordinary magnesium powder, apparently quite bright and free from oxide, was fractionally sifted, and the portion passing through between sieves of 90 and 60 meshes to the inch, respectively, was used. (0.0692 gave 0.3075  $\text{Mg}_2\text{P}_2\text{O}_7$ ; by Gibbs's method,  $\text{Mg}=97.03$ . 0.0258 gave 25.4 c.c.  $\text{H}_2$  [dry at 16.5° and 726 mm.]  $\text{Mg}=96.45$  per cent.) Only traces of aluminium and zinc could be detected in the substance. Since the phenomena investigated seemed to depend on the nature of the solutions and not on the small amounts of impurity in the magnesium, it was considered unnecessary to attempt any purification of this reagent.

*Sodium Chloride.*—Common salt was dissolved in distilled water, filtered, and the solution rendered just alkaline with sodium hydroxide and filtered again. The slightly alkaline solution was evaporated with continual stirring, and the first crop of crystals were well drained and kept over concentrated sulphuric acid.

*Water.*—Distilled water was redistilled in a glass still which had been previously well steamed out. This water was boiled under diminished pressure previous to being used.

*Hydrogen.*—This was prepared from zinc and pure sulphuric acid, and purified by passing through lead nitrate solution, silver nitrate solution, a soda-lime tower, and then a set of sodium hydroxide bulbs, and stored over water.

*Solutions.*—These were made up by weight. The number of molecules of water to each molecule of sodium chloride is represented by *c*.

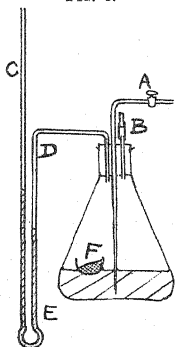
*Apparatus.*—At first the solution—10 cm. deep—was contained in a test-tube, and the hydrogen measured in a nitrometer, the volume being read every fifteen minutes.

The rate was constant in each case for about five hours. The

initial rate was read from the tangent to the curve, and reduced to c.c. at *N.T.P.* per gram of magnesium per hour.

In the second case, a conical flask was chosen as reaction vessel in order to have a smaller hydrostatic pressure on the magnesium. It was fitted with a rubber stopper carrying a delivery tube, *A* (Fig. 1), drawn to a point at the bottom of the flask, for the entry of hydrogen, an exit tube, *B*, which could be closed, and a water manometer, *C*, behind which was fixed a millimetre scale. Selected

FIG. 1.



quill tubing was used in making it, and it was carefully calibrated with distilled water at 25°, and found to be of uniform bore for the part calibrated, namely, the length *DE*. 1 cm. = 0.1880 c.c. at 25°. Twice distilled water saturated with hydrogen was used in the manometer. The weighed magnesium was floated on a capsule on the solution, the volume of which was always 25 c.c., and then the air displaced by, and the solution saturated with, hydrogen through *A* and *B* for not less than ten minutes, all being immersed in the bath. The apparatus was quickly shaken, and simultaneously a stop-watch was started. The volumes of hydrogen read off every half- or quarter-minute were reduced to *N.T.P.*, tabulated (table I), and plotted (Fig. 2, curves 1 and 2). The initial rate was obtained by drawing the tangent as shown. The kind of induction period at the start is much more pronounced with the more concentrated solutions, and is probably due to surface-tension effects, chiefly in the manometer.

TABLE I.

$c=30$ .

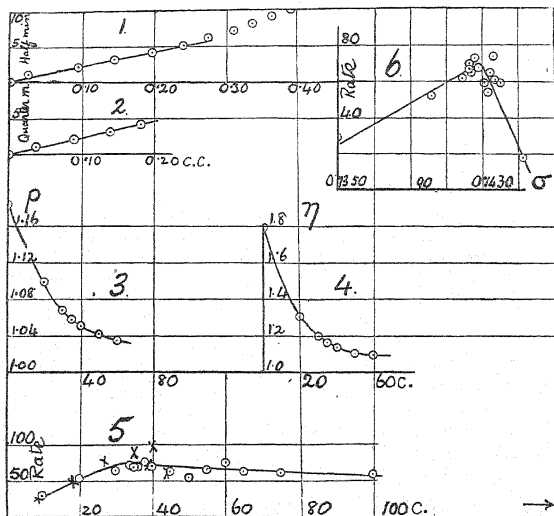
$\frac{1}{2}$ minute intervals.	Manometer, $\Delta$ (in cm.).	Hydrogen, c.c.	Total pressure (corr.).	Hydrogen, c.c. corrected.
0	0.6	0	—	0
1	0.9	0.15	753.9	0.0256
2	1.7	0.55	754.4	0.0941
3	2.3	0.85	754.9	0.1454
4	2.9	1.15	755.3	0.1969
5	3.4	1.40	755.7	0.2397
6	3.8	1.60	756.0	0.2742
7	4.2	1.80	756.3	0.3086
8	4.5	1.95	756.5	0.3344
9	4.8	2.10	756.7	0.3601
10	5.1	2.25	756.9	0.3860



TABLE I. (*continued*). $c = 38$ .

$\frac{1}{4}$ minute intervals.	Manometer, $\Delta$ (in cm.).	Hydrogen, c.c.	Total pressure (corr.).	Hydrogen, c.c. corrected.
0	0.36	0	—	0
1	0.78	0.21	754.0	0.0359
2	1.40	0.52	754.4	0.0889
3	1.98	0.81	754.9	0.1387
4	2.48	1.06	755.2	0.1814

FIG. 2.



The greatest precautions were taken that the solutions of sodium chloride were in each case quite free from acid. Immediately at the end of a determination they reacted alkaline.

The viscosities were determined with an Ostwald viscosimeter, the essential precautions being observed (Applebey, T., 1910, 97, 2000; from the equation

$$\eta = \eta_{\text{water}} \times \frac{\text{density of solution}}{\text{density of water}} \times \frac{\text{time of flow of solution}}{\text{time of flow of water}}$$

The densities were determined with a pycnometer, the weighings being carried out with a similarly treated counterpoise. These were as shown in table II. The curves are plotted in Fig. 2, 3 and 4.

TABLE II.

Concentration.	$\rho_{40}^{20}$ .	$\eta_{25}^{20}$ .
10	1.184	1.794
20	1.099	1.303
30	1.068	1.198
35	1.058	1.165
40	1.051	1.134
50	1.041	1.101
60	1.034	1.095

In table III are given the initial rates for the different concentrations of sodium chloride solutions.

TABLE III.

Time, hrs. min.	Temperature.	Pressure, mm.	Vol., c.c. (corr.)	Magnesium, c.	Gram.	Rate.	Remarks.
13 30	19°	762.3	31.32	9	0.0984	23.5	First method.
2 20	20	763.9	11.99	18	0.1069	48.1	
15	22	766.5	1.87	27	0.0995	75.1	Method not accurate enough.
1 20	25	758.7	8.32	45	0.1004	62.2	
16	24	758.3	2.29	35	0.0985	87.3	
15	22.5	766.1	2.42	40	0.1004	96.5	
15	23	767.1	1.58	44	0.1018	62.2	
16	23	768.3	1.87	39	0.0977	71.6	
4	25	749.5	0.72	30	0.1165	93.1	
7	25	749.8	0.18	30	0.0333	46.6	
3	24.1	749.9	0.45	30	0.1798	50.4	
2	19.2	749.2	0.51	30	0.1513	100.5	
1.5	20	749.2	0.37	30	0.1184	124.1	Second method. Better agreement.
0.5	25	749.4	0.0425	30	0.0840	60.7	
"	"	749.4	0.0710	30	0.1367	64.3	
"	"	750.5	0.0683	30	0.1248	62.3	
"	"	752.8	0.03845	10	0.1590	29.0	
"	"	752.9	0.0664	20	0.1531	52.1	
"	"	753.2	0.0479	30	0.1062	54.2	
"	"	754.8	0.0944	35	0.1702	66.6	
"	"	752.9	0.0684	40	0.1216	67.5	
0.25	"	752.3	0.0342	50	0.1507	54.4	
"	"	757.0	0.0417	60	0.1343	74.6	Quarter minute intervals.
0.5	"	753.4	0.0135	32	0.0955	17.0	
							Metal wetted accidentally during bubbling in hydrogen.
0.25	"	753.4	0.0513	34	0.1787	69.7	
"	"	753.4	0.0531	36	0.1940	65.7	
"	"	753.4	0.0454	38	0.1478	73.6	
"	"	754.8	0.0343	45	0.1412	59.5	
"	"	754.8	0.0411	55	0.1518	65.0	
"	"	754.8	0.0411	65	0.1581	62.4	
"	"	754.7	0.0386	75	0.1502	61.6	
"	"	755.2	0.0429	100	0.1722	59.7	
"	"	750.6	0.0148	$\infty$	0.1969	18.0	

Water only

These rates are plotted against concentrations in curve 5. The arrow indicates the rate for water ( $c=\infty$ ), and the crosses denote the values obtained with the nitrometer.

### Results.

No great accuracy can be claimed for the numerical values, chiefly because the assumption that the total area of equal weights of the sifted magnesium is constant is only approximately true. However, it is evident that curve 5 passes through a maximum at  $c=32$ ; also the surface density of water molecules in contact with magnesium (neglecting surface concentration effects) is given by  $\{c\rho/(cM_w + M_s)\}^{\frac{1}{2}}$ , where  $M_w$  is the molar weight of water,  $M_s$  that of sodium chloride, and  $\rho$  the density of the solution. Values of this expression ( $=\sigma$ ) have been found for various concentrations and then plotted against the corresponding rates in curve 6. This passes through a maximum for  $\sigma=0.1426$  about, or  $c=37$ . One would expect a maximum rate for  $c=\infty$ —pure water, since then the magnesium surface would be apparently open to attack by a denser population of water molecules. Again, the values of the viscosity, hydrostatic pressure, and surface tension (Forch, *Ann. Physik*, 1905, [iv], 17, 744) are each greater for  $c=32$  than for weaker solutions, so it seems that the maximum at  $c=32$  is not due to any special ease of expulsion of gas through the solution. Further, the specific conductivity of sodium chloride solutions steadily increases to a maximum at the saturation point, so that at  $c=32$  the conductivity is not best suited for electrolytic action of impurities in the magnesium to take place.

### Conclusions.

(1) Both alkaline and neutral salts positively catalyse the reaction between ordinary magnesium and purified water at the ordinary temperature.

(2) With sodium chloride solutions, the rate of evolution of hydrogen depends on the concentration, the differences being easily detected by the eye. The initial rates for approximately equal areas of magnesium in contact with different concentrations of sodium chloride solutions have been measured, and a maximum has been found for a solution of 32 molecules of water per molecule of sodium chloride.

(3) It is considered that the existence of this maximum points to a specific effect of the dissolved sodium chloride on the water.

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XXIX.—*The Theory of Duplex Affinity.*

By SAMUEL HENRY CLIFFORD BRIGGS.

IN a former paper (T., 1908, 93, 1564) it was shown how the old conception of duplex affinity can be applied in devising constitutional formulæ for complex inorganic compounds. In a subsequent paper (*ibid.*, 1917, 111, 253), the theory of duplex affinity was treated from the point of view of the electrical structure of matter. It was assumed that every element is able to exert both positive and negative affinity, positive affinity being a tendency to lose electrons and negative affinity a tendency to attract electrons. A further distinction was made between primary and secondary affinity, the secondary affinity being opposite in sign to the primary affinity, and only coming into action after the primary affinity has been satisfied. By means of these assumptions, it was possible to correlate a number of apparently disconnected phenomena, including the structure and stability of complex compounds, the strength of acids and bases, polymerisation, etc.

The present communication is concerned more particularly with secondary affinity, and some conclusions have been reached which have made it possible to apply the theory of duplex affinity in several new directions.

*Secondary Negative Affinity and Secondary Positive Affinity.*

As in the previous paper (T., 1917, 111, 253), Lodge's view (*Nature*, 1904, 70, 176) that the electrons in an atom are bound to the positive charge, not by a single line of attraction or elastic thread, but by a bundle of a very large number of lines of force, is adopted. For the sake of simplicity, it is supposed that the atoms are spheres, although this is not an essential feature of the general argument. The volumes of the atomic spheres are assumed to be directly proportional to the so-called atomic volumes of the elements.

The term "valency" is used in this paper in a strictly electrochemical sense, in accordance with Sir J. J. Thomson's theory (*Phil. Mag.*, 1914, [vi], 27, 757).

Consider the case of two univalent atoms *A* and *B*, which combine to form a compound *AB* as the result of the transfer of an electron from *A* to *B*, *A* having positive primary affinity and *B* having negative primary affinity. Owing to the attraction of *B* for the electron, a number of lines of force which united the

electron to the positive nucleus of the atom  $A$  are broken. Call this number  $u$ . Then in the atom  $B$ ,  $u$  lines of force joining electrons in the atom  $B$  (previous to its combination with  $A$ ) to its positive nucleus will be loosened, as a result of the passage of the electron from  $A$  to  $B$ . Suppose, now, that the compound  $AB$  undergoes electrolytic dissociation in solution into the ions  $A^+$  and  $B^-$ . The positive nucleus of the cation  $A^+$  will be able to bind  $u$  lines of force from electrons in other atoms, that is to say, the cation  $A^+$  will have negative affinity, and in this way the secondary negative affinity of the element  $A$  arises. The electrons in the anion  $B^-$ , on the other hand, will have  $u$  lines of force loosened, and therefore be able to attach themselves to the positive nuclei of other atoms. Consequently, the anion  $B^-$  has positive affinity, which is the secondary positive affinity of the element  $B$ .

Attention must now be directed to a fundamental difference between secondary negative affinity and secondary positive affinity. According to the modern views on the electrical structure of matter, the positive nucleus is situated at the centre of the atom, and its spatial dimensions are extremely minute compared with the volume of the atom as a whole. As we have seen above, however, secondary negative affinity arises from the power of the nucleus to attract lines of force (or electrons). Since the nucleus is at the centre and is so exceedingly small, it follows, so far as the effect on other atoms is concerned, that secondary negative affinity may be regarded as an attractive force distributed equally over the surface of the atomic sphere.

Secondary positive affinity, on the other hand, emanates from the outer electrons (valency electrons or mobile corpuscles) in the atom. The secondary positive affinity cannot therefore be regarded as being equally distributed over the atomic sphere, but must be confined to certain individual electrons or rings of electrons. In other words, secondary negative affinity conforms to Werner's theory of affinity ("*Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*," 3rd ed., p. 83), whereas secondary positive affinity does not. This difference between secondary negative affinity and secondary positive affinity appears to be of considerable importance in the building up of inorganic compounds, as will be more clearly seen below.

When the ions  $A^+$  and  $B^-$  combine to form the molecule  $AB$ , some of the loosened lines of force in  $B$  will be attached to the positive nucleus of  $A$ , as shown by the "ionic formula"  $\rightarrow A^+ \leftarrow B^- \rightarrow$  (T., 1917, 111, 253). If the number of lines of force thus attached is denoted by  $v$ , then in the compound  $AB$  the positive nucleus of  $A$  is still able to bind  $u-v$  lines of force,

whereas the electrons in  $B$  have still  $u-v$  lines of force loosened and capable of attachment to the nuclei of other atoms. The number  $u-v$ , therefore, represents the unsaturated secondary negative affinity of  $A$  and the unsaturated secondary positive affinity of  $B$ , indicated by the dotted arrows in the "atomic formula"  $\cdots A \rightarrow B \cdots$  and in the "ionic formula"  $\cdots A' \leftarrow B' \cdots$  (T., 1917, 111, 253).\*

### *Influence of Atomic Volume.*

Since the secondary negative affinity is distributed equally over the surface of the atomic sphere, it follows that when the atomic volume is large,  $v$  will be correspondingly small and  $u-v$  proportionately large (see p. 286). When the compound  $AB$  is dissolved in a dissociating medium, such as water, the molecules of the solvent combine with  $A$  and  $B$  by means of the unsaturated secondary affinity, thereby bringing about dissociation into the ions  $A'$  and  $B'$  (compare T., 1908, 93, 1564). Therefore, if  $u-v$  is large,  $AB$  will be a strong electrolyte. As shown above, however,  $u-v$  is large when the atomic volume of  $A$  is large, and this is the reason why the salts of the alkali metals are the strongest electrolytes.

On the other hand, although when the atomic volume of  $A$  is large the total unsaturated affinity is correspondingly large, nevertheless the *intensity* of the affinity per unit area of the atomic sphere varies *inversely* as the square of the radius, and is therefore large when the atomic volume of  $A$  is small. Consequently, the molecular compounds  $(nM \cdot A)B$ , formed by satisfying the free secondary negative affinity of  $A$  by the free secondary positive affinity of  $n$  molecules of a compound  $M$  (such as ammonia or water) (T., 1917, 111, 253), will be most clearly defined and stable

\* Three types of combination are distinguished: (1) Combination due to primary affinity only, as in the formula  $\cdots A \rightarrow B \cdots$ , the passage of the electron from  $A$  to  $B$  being indicated by the thick arrow pointing from  $A$  to  $B$ . (2) Combination due to secondary affinity only as seen in molecular compounds, such as  $2H_3N \rightarrow CuCl$ , the union of the electrons in the nitrogen atom to the positive nucleus of the copper atom being indicated by the thin arrow pointing from nitrogen to copper. (3) Combination due to both primary and secondary affinity as in the non-polar compound  $A \rightleftharpoons B$ .

It should be noted that the formulæ  $\cdots A \rightarrow B \cdots$  and  $A \rightleftharpoons B$  represent the limiting cases of the strongest possible electrolyte and the truly non-polar compound respectively. Most compounds will come in between the two formulæ. A compound of intermediate properties might therefore be written  $\cdots A \rightleftharpoons B \cdots$ , but it is often convenient to write it as a compound of charged ions rather than of atoms, and in this way the "ionic formula"  $\cdots A' \leftarrow B' \cdots$  is derived.

when the volume of  $A$  is small. As a matter of fact, those elements which form the most stable complex compounds are all found in the depressions of the atomic volume curve (chromium, manganese, iron, cobalt, nickel, copper, zinc, ruthenium, palladium, rhodium, silver, osmium, platinum, iridium, and gold) (see also the work of Ephraim on the effect of the atomic volume of the central atom on the stability of metal-ammonia compounds, *Ber.*, 1912, 45, 1322).

Conversely, the same reasoning elucidates the somewhat contradictory phenomenon that many of the salts of the alkali metals which are readily soluble in water separate from solution in the anhydrous state. These salts dissolve readily, because of the large value of  $u-v$ . They do not give stable hydrates, because of the small intensity of the affinity per unit area of the atomic sphere which results from the large atomic volume of the alkali metals.

#### *Non-polar Compounds.*

If the two ions  $A'$  and  $B'$  were to combine in such a way that the secondary affinities completely saturated each other, then the electron would be pulled back into  $A$  and the atoms would be held in combination by means of two equal bundles of lines of force, one passing from the nucleus of  $A$  to the electrons of  $B$ , and the other from the nucleus of  $B$  to the electrons in  $A$ . That is to say,  $AB$  would be a non-polar compound, as shown by the formula  $A \equiv B$ .

The conception of secondary negative affinity developed above (p. 279) leads to the following conclusions with regard to the conditions for the formation of non-polar compounds in those cases in which the valency of the element  $A$  with primary positive affinity is fully saturated. The conclusions do not, however, apply when  $A$  is not exerting its full valency, as the mobile corpuscles still remaining on  $A$  introduce complications.

The compounds to be considered, therefore, are those represented by the formula  $AB_x$ , in which  $x$  varies from 1 to 8 when  $B$  is a univalent atom.

When  $x=1$ , the secondary negative affinity of  $A$  is only partly saturated, as already explained (p. 280), because only a part of the spherical surface of  $A$  comes under the influence of  $B$ . If  $x=2$ , and  $A$  is therefore united to two atoms of  $B$ , a larger part of the spherical surface of  $A$  is affected, and in general as  $x$  increases, more and more of the spherical surface of  $A$  is brought under the influence of  $B$ . Hence as  $x$  increases, the tendency of  $AB_x$  to undergo electrolytic dissociation decreases (see p. 280).

The salts of the metals in the earlier groups of the periodic table are therefore the strongest electrolytes, and the electrolytic properties become less marked in the compounds of the metals with higher valency (when they are exerting their full valency).

If, however,  $AB_x$  is to be a truly non-polar compound, the secondary negative affinity of  $A$ , which is distributed equally over the surface of the atomic sphere, must be completely saturated, and the optimum condition for such complete saturation will be reached when the atoms of  $B$  are symmetrically distributed in space around the spherical surface of  $A$ .

Since the maximum valency is 8, the number of cases of symmetrical distribution is strictly limited. If  $B$  is univalent,  $x$  may be 4, 6, or 8, when the atoms of  $B$  will be distributed around the spherical surface of  $A$  at the corners of a regular tetrahedron, a regular octahedron, and a cube respectively. If  $B$  is bivalent, the only possible case is  $x=4$ , when the  $B$  atoms are situated at the corners of a regular tetrahedron. We should therefore expect to find the non-polar properties most strongly marked in compounds having the formulæ  $AB_4$ ,  $AB_6$ , and  $AB_8$  when  $B$  is univalent, and  $AB_4$  when  $B$  is bivalent.

Since the forces between the molecules of non-polar compounds are small (Thomson, *loc. cit.*, p. 760), such compounds, in addition to their inability to undergo electrolytic dissociation, will also be comparatively volatile and more or less inert. There are several striking instances of compounds with these characteristics in the four classes of substances under discussion.

In the group  $AB_4$  we have the typically non-polar compounds, methane and carbon tetrachloride.

The formula  $AB_6$  is represented by the gaseous sulphur hexafluoride,  $SF_6$ , which is almost as inert as nitrogen (Moissan and Lebeau, *Compt. rend.*, 1900, **130**, 865, 984; Berthelot, *Ann. Chim. Phys.*, 1900, [vii], **21**, 205), and by the gaseous tungsten hexafluoride (Ruff and Eisner, *Ber.*, 1905, **38**, 742),  $WF_6$ .

Only one compound of the formula  $AB_8$  has hitherto been prepared. This is osmium octafluoride (Ruff and Tschirsch, *Ber.*, 1913, **46**, 929), which boils below  $50^\circ$ , and is a highly stable although reactive substance.

The class  $AB_4$ , in which  $B$  is bivalent, includes the remarkable tetroxides of ruthenium and osmium,  $RuO_4$  and  $OsO_4$ . These compounds both boil at about  $100^\circ$ , and are so completely saturated that they are incapable of combination with alkali hydroxides. Indeed, osmium tetroxide can be distilled off from its solution to which an alkali has been added (compare Ostwald, "The Principles of Inorganic Chemistry," p. 757).



Although symmetry of structure is thus often associated with, and conduces to, non-polarity, it does not follow that all symmetrical compounds will be without polarity, as other factors, such as the relative atomic volumes of  $A$  and  $B$ , will also exert an influence.

Conversely, when  $A$  is *not* exerting its full valency, non-polar combination is possible in substances which are not spatially symmetrical. Thus, according to Thomson (*loc. cit.*), carbon monoxide and nitrous oxide are non-polar compounds.

Other examples given by Thomson bring out the relationship between symmetry and non-polarity in another way. Although both carbon tetrachloride,  $\text{CCl}_4$ , and methane,  $\text{CH}_4$ , are truly non-polar, nevertheless chloroform,  $\text{CHCl}_3$ , and methyl chloride,  $\text{CH}_3\text{Cl}$ , are polar compounds.

#### *Werner's Co-ordination Numbers and the Co-ordination Formula.*

Suppose the cation  $A'$  combines with  $n$  molecules of a compound  $M$  possessing free secondary positive affinity, such as ammonia or water, to give the complex ion  $(nM.A)'$ . Here also the conditions for maximum saturation of the secondary negative affinity of  $A$  will involve spatial symmetry in precisely the same way as was seen to apply in the formation of non-polar compounds. The maximum value of  $n$  should therefore be either 4, 6, or 8, according to the relative volumes of the atom  $A$  and the molecule  $M$ ; but the maximum value of  $n$  is the maximum co-ordination number of the element  $A$ , and Werner (*loc. cit.*, p. 52) has shown that this is either 4, 6, or 8. It would appear, also, that the geometrical relationship existing between the volumes of the central atom  $A$  and the molecule  $M$  is of more importance than the intensity of the affinity in determining the value of the co-ordination number. We find, for example, that barium, with a comparatively large atomic volume, has the maximum co-ordination number 8, as seen in the compound,  $(\text{Ba}8\text{NH}_3)\text{Cl}_2$ , whereas cobalt, with a much smaller atomic volume, has the maximum co-ordination number 6 in the compound  $(\text{Co}6\text{NH}_3)\text{Cl}_3$ , in spite of the fact that cobaltic salts have a much greater tendency to combine with ammonia than is shown by barium salts. Similarly, boron, with a very small atomic volume, has the maximum co-ordination number 4 in the compound  $(\text{BF}_4)\text{H}$ .

Attention must now be directed to the limiting case in which the secondary negative affinity of  $A$  is *completely* saturated by the free positive affinity of  $M$ , giving the complex ion  $(nM.A)'$ . In what way will the anion  $B'$  combine with this complex cation to

give the molecule  $(nM.A)B$ ? In discussing this question, we may suppose that  $M$  is a molecule of ammonia. In the former papers (T., 1908, 93, 1564; 1917, 111, 253), ammonia was written



This formula was derived from the facts (1) that the hydrogen atoms do not undergo electrolytic dissociation in solution in water, and therefore have both primary and secondary affinity saturated, and (2) that the nitrogen atom has free secondary positive affinity, as shown by the ease with which ammonia molecules can combine with the free secondary negative affinity of metals in their salts to give metal-ammonia compounds. From the reasoning developed above, however (p. 280), it is clear that this formula for ammonia, although correct so far as it goes, is not quite complete, because if the nitrogen atom still has  $u-v$  lines of force loosened, as expressed by the dotted arrow, then each hydrogen atom must be able to bind  $\frac{u-v}{3}$  lines of force to its nucleus. In other words, each

hydrogen atom has still a little free secondary negative affinity. Since, however, the free secondary positive affinity in the ammonia molecule is confined to one atom only (the nitrogen atom), it masks the free secondary negative affinity which is distributed over the three hydrogen atoms. In the general case of a compound  $A_mB_n$ , in which  $A$  and  $B$  have free secondary affinity, if  $m$  is greater than  $n$  the molecule  $A_mB_n$  will react as if it had the free secondary affinity of  $B$  only. This characteristic will be the more strongly marked the greater the difference between  $m$  and  $n$ , and it will be all the more intensified the greater the volume of  $A$  (the atom with primary positive affinity), and vice versa. Thus we find that ammonia, water, and potassium chloride react as if they had free secondary positive affinity only in forming complex compounds, whereas cupric chloride, ferric chloride, etc., behave like substances with free secondary negative affinity.

The complete formula for ammonia should therefore be written



in which each hydrogen atom has a little free secondary negative affinity. Returning now to the combination of the complex  $(nM.A)^+$  with the anion  $B^-$  to give the salt  $(nM.A)B$ , we may take the concrete case in which the complex is  $(\text{Co}6\text{NH}_3)^{+++}$  and the anion is  $\text{Cl}^-$ , and assume that the secondary negative affinity of the cobalt atom is *completely* saturated by the free secondary positive affinity of the nitrogen in the six molecules of ammonia.

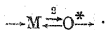
The only possible way in which the chloride ions can unite with the complex to give the salt  $(\text{Co}_6\text{NH}_3)\text{Cl}_3$  is by the saturation of the free secondary negative affinity of the eighteen hydrogen atoms by the positive affinity of the chlorine ions. This gives Werner's co-ordination formula  $(\text{Co}_6\text{NH}_3)\text{Cl}_3$  exactly, in which, according to Werner's phraseology, the chlorine atoms are united to the outer sphere of the complex.

It should be carefully noted, however, that the co-ordination formula only applies to the *limiting* case in which the secondary negative affinity of  $A$  is *completely* saturated by  $nM$  in the complex  $(nM.A)'$ . If this saturation is not complete, then the positive nucleus of  $A$  will exert an attraction on the electrons in  $B$ , as shown by the "ionic formula"  $nM \rightarrow A' \leftarrow B' \rightarrow$  (T., 1917, 111, 260). A familiar example is seen in aquopentammine cobaltic chloride,  $(\text{Co}^{\text{5NH}_3}_{\text{H}_2\text{O}})\text{Cl}_3$ , which changes spontaneously into chloropentammine cobaltic chloride,  $(\text{Co}^{\text{5NH}_3}_{\text{Cl}})\text{Cl}_2$ . Unless the cobalt atom exerts a direct attraction on the chlorine atoms, as shown by the formula  $\text{5NH}_3 \text{---} \text{Co}^{\text{---}} \text{---} \text{Cl}_3^{\text{---}} \rightarrow$ , it is impossible to understand this spontaneous change.

#### *Application of the Theory of Duplex Affinity to Oxygen Compounds.*

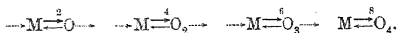
In the former papers (*loc. cit.*), most of the examples considered were halogen compounds. The development of the theory of secondary negative affinity in the present communication has made it possible to study oxygen compounds from the point of view of duplex affinity in such a way as to bring out some general relationships which are not touched on by other theories of affinity and valency.

Take the case of a metal,  $M$ , which forms a series of oxides,  $\text{MO}$ ,  $\text{MO}_2$ ,  $\text{MO}_3$ ,  $\text{MO}_4$ . In the oxide  $\text{MO}$ , in which the oxygen atom has received two electrons from the atom  $M$ , only part of the atomic sphere of  $M$  will come under the influence of the oxygen atom. Hence the secondary affinity of both atoms will be partly unsaturated, and the formula will be



\* Instead of denoting the passage of two electrons by two thick arrows  $\text{M} \rightleftharpoons \text{O}$ , it is more convenient to write one arrow only, with a small figure above to express the number of electrons which it represents, for example,  $\text{M} \overset{2}{\rightarrow} \text{O}$ .

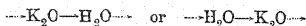
When MO is oxidised to give  $\text{MO}_2$ , a greater part of the spherical surface of M will come under the influence of the oxygen atoms, and the saturation of the secondary affinity will be more complete than in the first oxide, MO. This will apply still more in  $\text{MO}_3$ , and most of all in  $\text{MO}_4$ , in which the oxygen atoms are distributed symmetrically in space around M. In  $\text{MO}_4$  we therefore have the possibility of complete saturation of the secondary affinity with the production of a non-polar compound. The oxides  $\text{OsO}_4$  and  $\text{RuO}_4$ , referred to above (p. 282), appear to approximate closely to this condition. The four oxides should therefore be written (assuming that  $\text{MO}_4$  is non-polar):



It may perhaps be better to write the non-polar oxide  $\text{M} \overset{8}{\text{=}} \text{O}_4$ , rather than  $\text{M} \overset{8}{\text{=}} \text{O}_4$ , as the electrons will not have left the M atom in this case.

It should be carefully noted that, since the secondary affinity of M is increased by each addition of an oxygen atom, the saturation of the secondary affinity of the first oxygen atom becomes more complete as oxidation proceeds, because, the secondary affinity of M being distributed equally over the surface of the atomic sphere, the intensity of the affinity present on that part of the spherical surface which comes under the influence of the first oxygen atom will increase with increase in the number of oxygen atoms combined. The *free* secondary affinity of the first oxygen atom will therefore decrease with increasing oxidation of M until in the final, non-polar stage the secondary affinity of the first oxygen atom will be completely saturated. The same reasoning applies, of course, to all the other oxygen atoms as well.

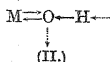
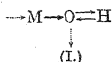
*The Hydration of Oxides.*—When potassium oxide and water are brought together, there are two ways in which combination may occur. The strongly marked, free secondary positive affinity of the oxygen atom in the potassium oxide may attract the hydrogen atoms of the water, which have slight, unsaturated secondary negative affinity, or the unsaturated secondary negative affinity of the potassium may combine with the slight, free secondary positive affinity of the oxygen atom in the water molecule. We may therefore obtain



or perhaps a ring structure  $\text{K}_2 \overset{\text{O} \text{---} \text{H}_2}{\text{---} \text{O}}$ . In potassium,  $u-v$  is large, owing to the large atomic volume of potassium (see p. 280), and therefore the unsaturated secondary affinities of the potassium

atoms and the oxygen atoms are large. In water, on the other hand,  $u-v$  is small (as seen from the very slight extent to which it is dissociated into hydrogen and hydroxyl ions); hence the unsaturated secondary affinities of the hydrogen atoms and the oxygen atom are small. In each of the three formulæ for  $K_2O, H_2O$ , we consequently have the two potassium atoms electrically equal, the two hydrogen atoms electrically equivalent, but the two oxygen atoms very different from each other. The tendency will be for the affinities to be redistributed in such a way as to make the two oxygen atoms also electrically equal, and we therefore have the change  $K_2O, H_2O \rightleftharpoons 2KOH$ . Similar considerations will apply to the hydration of other oxides.

*Bases and Acids.*—When an oxide is hydrated, the product may be either a base or an acid, according to the manner in which it undergoes electrolytic dissociation in solution. If  $MOH$  were a base of the strongest possible type, the formula would be written as (I), and if it were the strongest possible type of acid, as (II) (T., 1917, 111, 253).



It has already been shown (p. 286) that increase in the number of oxygen atoms implies a more complete saturation of the secondary affinity of all the oxygen atoms already present in the oxide (anhydrous or hydrated). As the secondary affinity of the oxygen atom of the hydroxyl group becomes more completely saturated by the secondary affinity of  $M$ , there is less affinity left to saturate the secondary affinity of the hydrogen of the hydroxyl group, and the free secondary affinity of the hydrogen therefore increases. Consequently, the tendency of the hydrogen atom to be electrolytically dissociated becomes greater, and the structure of the hydroxyl group changes from  $\rightarrow O \rightleftharpoons H$  (basic) to

$\rightleftharpoons O \leftarrow H \leftarrow$  (acidic), with increase in the number of oxygen atoms

united to the element  $M$ . We therefore have the following general rule:

When a series of oxides of the same element  $M$  are hydrated, the hydrate of the highest oxide is the strongest acid (or weakest base). In other words, in a series  $M \overset{OH}{O_x}$  the greater the value of  $x$  the stronger the acidic properties (or the weaker the basic properties).

This rule appears to hold good throughout the periodic table. It is exemplified most clearly in the compounds of the elements in the sixth, seventh, and eighth groups, these being the elements which exhibit the most numerous stages of oxidation. Thus ferrous oxide is basic, ferric oxide less basic (as shown by the greater ease with which ferric salts are hydrolysed), and iron trioxide is acidic. The oxides of chromium form a similar series from the basic chromous and chromic oxides to the acidic chromium trioxide. Manganous oxide is basic, manganic oxide less basic, and manganese dioxide not definitely basic or acidic, whereas manganese trioxide is acidic and dimanganic heptoxide strongly acidic.

The oxides of chlorine give rise to a series of acids increasing in strength from the very weak hypochlorous acid,  $\text{HOCl}$ , to the strong chloric and perchloric acids,  $\text{HClO}_2$  and  $\text{HClO}_3$ . Among nitrogen compounds, hyponitrous acid is very weak, nitrous acid is stronger, and nitric acid is one of the strongest acids known.

The fact that ruthenium and osmium tetroxides are not acidic, although diruthenium heptoxide is strongly acidic, is only an apparent exception to the rule. Owing to their highly saturated character, as has already been shown (p. 282), these compounds are incapable of combination with water, and cannot therefore give rise to hydrated oxides. They therefore do not come within the scope of the rule which applies to hydrated oxides only.

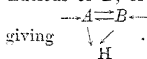
#### *The Hydrogen Ion and the Catalytic Activity of Acids.*

From the point of view of the theory of duplex affinity, the hydrogen atom is particularly interesting. According to the views of van den Broek and others (*Ann. Reports*, 1913, 10, 271), the hydrogen atom is built up of a positive nucleus and one electron (compare Allen, T., 1918, 113, 390). Consequently, the hydrogen ion  $\text{H}^+$  must consist of a positive nucleus only. The secondary negative affinity of the hydrogen ion must therefore be considered to be concentrated in a "point" of nuclear dimensions rather than distributed over the surface of a (comparatively) very large sphere. The conclusions which have been arrived at in the above discussion from the consideration of the atomic sphere will therefore not necessarily apply to hydrogen. Thus it is not essential for the production of non-polar compounds that the hydrogen atom should be surrounded by negative atoms, as in the cases of sulphur and osmium, for example (see p. 282), methane being a typical non-polar compound.

The identity of the hydrogen ion with the positive nucleus of the hydrogen atom may perhaps ultimately furnish a rational ex-

planation of the catalytic activity of acids, somewhat on the following lines.

Take a molecule  $A \equiv B$  with a tendency to dissociate according to the equation  $AB \rightleftharpoons A + B$ . A hydrogen ion (nucleus) if brought into contact with such a molecule will attract to itself some of the lines of force joining the electrons in  $A$  to the positive nucleus of  $B$ , or the electrons in  $B$  to the positive nucleus of  $A$ ,



The bond uniting  $A$  to  $B$  will therefore become weaker, and the tendency of  $AB$  to dissociate will be increased. It is consequently to be expected that the hydrogen ion will accelerate a chemical change which is already taking place, or even induce a change which would not otherwise occur. Theoretically speaking, other positive ions should act in a similar manner; but since the secondary negative affinity of all other elements is distributed over the surface of a comparatively very large sphere instead of being concentrated in a "point" of nuclear dimension, the catalytic activity of other cations will be exceedingly small compared with that of hydrogen ions.

According to the theory of acids developed in the former paper (T., 1917, 111, 253), if we neglect unsaturated affinity, the general formula for acids may be written  $H \rightleftharpoons X$ . If  $x$  is the value of the saturated primary affinities and  $y$  the value of the saturated secondary affinities in the formula  $H \rightleftharpoons X$ ,  $y$  may vary from  $y = x$  (the weakest possible acid) to  $y = 0$  (the strongest possible acid).

If we now write the formulæ to show the unsaturated affinities, the strongest possible acid has the formula (I) and the weakest possible acid the formula (II).



The formula (I) is the case where  $v$  (see p. 279) is vanishingly small. Strictly speaking, it is the formula of the dissociated acid ( $v = 0$ ). The unsaturated secondary negative affinity of the hydrogen atom in a molecule of the strongest possible acid (I) is therefore equal to that of the hydrogen ion itself, and as we pass down the series through acids of decreasing strength, the unsaturated secondary negative affinity of the hydrogen atom becomes less until it vanishes, as seen in formula (II). It therefore follows that the undissociated molecule of a very strong acid should also exert catalytic activity, which catalytic activity should decrease

with decreasing strength of the acid, becoming zero in the weakest possible acid (II). It has been shown experimentally that the undissociated molecule of an acid has catalytic activity, the activity diminishing with decreasing strength of the acid (Goldschmidt and Thuesen, *Zeitsch. physikal. Chem.*, 1912, **81**, 39; Dawson and Powis, T., 1913, **103**, 2135; Dawson and Reiman, *ibid.*, 1915, **107**, 1426; Snethlage, *Zeitsch. physikal. Chem.*, 1913, **85**, 211), but according to Dawson and Powis, the activity of the undissociated acid in some cases is much greater than that of the hydrogen ion. In considering this question, it is necessary to take into account the effect of solvation.

According to the theory of duplex affinity, the chief cause of electrolytic dissociation is the combination of solute and solvent by means of unsaturated secondary affinity (see p. 280). In a solution of an acid we therefore have the following equilibria:

Undissociated molecule + solvent  $\rightleftharpoons$  solvated molecule.

Solvated molecule  $\rightleftharpoons$  solvated hydrogen ion + solvated anion.

Solvated hydrogen ion  $\rightleftharpoons$  solvent + hydrogen ion.

Solvated anion  $\rightleftharpoons$  solvent + anion.

Hydrogen ion + anion  $\rightleftharpoons$  undissociated molecule of acid.

Take now the extreme case in which the secondary negative affinity of the hydrogen ion is completely saturated by the secondary positive affinity of  $n$  molecules of the solvent  $S$  (as in a very basic liquid) to give the complex ion  $nS.H^+$ . The positive charge will now be distributed over the comparatively very large outer sphere of the complex (compare p. 284) instead of being concentrated in the nucleus of the hydrogen ion, and the catalytic activity of the complex will therefore be comparatively very small. Solvation will therefore reduce the catalytic activity of both hydrogen ion and undissociated molecule, and the observed catalytic activity of the hydrogen ion and the undissociated molecule in any given experiment will not be proportional to the real catalytic activity of each when unsolvated, but will depend on the degree of solvation of acid and hydrogen ion in accordance with the above-mentioned equilibria. Again, if the solvation is slight, the solvated ion and the solvated molecule may also have appreciable catalytic activity.

These principles are in agreement with the experimental observations on the relative catalytic activities of acids in different media. Water forms complexes much more readily than alcohol; therefore in aqueous solution solvation should be greater than in alcoholic solution, and the catalytic activity of acids should be less in water than in alcohol (compare Kistiakowski, *Zeitsch. physikal. Chem.*,



1898, 27, 253, and especially Dawson, T., 1911, 99, 1). Dawson has found that in alcoholic solutions the catalytic activity may be one hundred times as great as in water. Further, the addition of water has been found to decrease the catalytic activity in alcoholic solutions, and this has been shown to be due to combination of the water with the hydrogen ions (Goldschmidt and Udby, *Zeitsch. physikal. Chem.*, 1907, 60, 728; Lapworth, T., 1915, 107, 857).

It would be of considerable interest from the point of view of this paper if experiments could be made on the catalytic activity of acids in some truly non-polar medium, such as benzene or carbon tetrachloride. In such a medium, solvation and ionisation would be reduced to a minimum, because non-polar compounds are fully saturated, and therefore unable to combine with the solute. It has been shown, for instance, that benzene at 18° dissolves 2 per cent. of its weight of hydrogen chloride, and that the solution is without electrical conductivity (Falk and Walker, *Amer. Chem. J.*, 1904, 31, 398). The catalytic activity in a truly non-polar medium would therefore be due to the unsolvated molecule only, and in the case of a very strong acid would probably be very great compared with the activity of the undissociated molecule in aqueous or alcoholic solution.

### Conclusion.

For the sake of simplicity, it has been assumed throughout this paper that the atoms are spheres. It must be emphasised, in conclusion, however, that the atomic sphere so often referred to is a purely geometrical conception. We may suppose it to be a sphere described around the atom with the positive nucleus at the centre, and the radius sufficient to include all the constituents of the atom (valency electrons, etc.) within the sphere. The use of this conception is justified by the atomic volume relationships of the elements, and by the fact that the atoms are not capable of interpenetration when endowed with such small amounts of energy as correspond with the motions of thermal agitation of molecules (compare R. A. Millikan, "The Electron," pp. 139, 191).

[Received, October 23rd, 1918.]

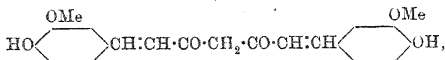
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XXX.—*Curcumin.*

By PRAPHULLA CHANDRA GHOSH.

THE work described in this paper was in progress, and in fact completed, before an account of the synthesis of curcumin by Lampe (*Ber.*, 1918, **51**, 1347) appeared.

A portion of the work was devoted to proving the presence of the  $\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot$  group, which in any case is now clear from the synthesis, confirming the formula,



previously put forward by Milobendzki, Kostanecki, and Lampe (*Ber.*, 1910, **43**, 2163). The results bearing on this point are therefore given in an exceedingly abbreviated form.

With benzaldehyde, curcumin forms a benzylidene derivative, and it also forms a condensation product with nitrosodimethylaniline.

The action of bromine on curcumin and some of its derivatives was also studied with the object of testing the presence of two double bonds.

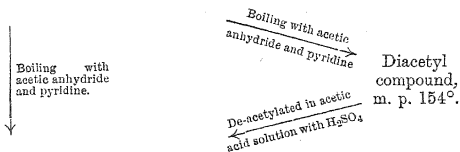
There were obtained *monobromocurcumin*,  $\text{C}_{21}\text{H}_{19}\text{O}_6\text{Br}$ , *monobromodicarbethoxycurcumin*,  $\text{C}_{21}\text{H}_{17}\text{O}_4\text{Br}(\text{O}\cdot\text{CO}_2\text{Et})_2$ , *monobromodicarbethoxycurcumin tetrabromide*,  $\text{C}_{21}\text{H}_{17}\text{O}_4\text{Br}_5(\text{O}\cdot\text{CO}_2\text{Et})_2$ , *dibromodicarbethoxycurcumin tetrabromide*,  $\text{C}_{21}\text{H}_{16}\text{O}_4\text{Br}_6(\text{O}\cdot\text{CO}_2\text{Et})_2$ , *monobromodiacetylcurcumin*,  $\text{C}_{21}\text{H}_{17}\text{O}_4\text{Br}(\text{OAc})_2$ , *dibromodiacetylcurcumin tetrabromide*,  $\text{C}_{21}\text{H}_{16}\text{O}_4\text{Br}_6(\text{OAc})_2$ , *monobromodimethylcurcumin*,  $\text{C}_{21}\text{H}_{17}\text{O}_4\text{Br}(\text{OMe})_2$ , and *dibromodimethylcurcumin tetrabromide*,  $\text{C}_{21}\text{H}_{16}\text{O}_4\text{Br}_6(\text{OMe})_2$ .

In the course of this investigation, it was discovered that dicarbethoxycurcumin could be converted into dicarbethoxy*isocurcumin* simply by boiling with acetic anhydride and pyridine. This led to the view that one of the two known diacetyl derivatives of curcumin was probably diacetyl*isocurcumin*. Ciamician and Silber described a diacetylcurcumin melting at  $169\text{--}170^\circ$ , whilst Jackson prepared an isomeric substance melting at  $154^\circ$  by acetylating curcumin with acetic anhydride and sodium acetate. It was suspected that the latter was probably diacetyl*isocurcumin*, and this suspicion was found to be correct.

Jackson's compound, which can also be formed by acetylating curcumin with acetic anhydride and pyridine, gives Heller's *isocurcumin* (*Ber.*, 1918, **47**, 887) on hydrolysis. It is therefore quite

easy to convert curcumin into *isocurcumin*. These reactions can be represented graphically, thus:

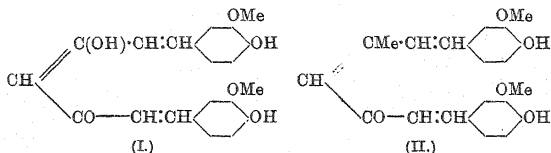
Dicarbethoxycurcumin ← Curcumin



Dicarbethoxyisocurcumin ← *iso*Curcumin.

This simple conversion of curcumin into *isocurcumin* confirms Heller's view that the two substances are geometrical isomerides.

From the ferric chloride reaction, Heller considers that curcumin exists in the enolic form (I), and as there is considerable



resemblance between this formula and that of *divanillylidene-mesityl oxide* (II), the latter has been prepared in the course of this investigation by condensing two molecular proportions of vanillin with one of mesityl oxide by means of hydrochloric acid, and it is intended to compare the absorption spectra of this substance with that of curcumin; similarity of absorption spectra would speak in favour of similarity of molecular configuration.

The condensation of mesityl oxide with some other aromatic aldehydes has been studied, and *p*-hydroxybenzylidenemesityl oxide, *o*-hydroxybenzylidenemesityl oxide, *p*-peronylidene-mesityl oxide, and *cinnamylidenemesityl oxide* have been isolated.

In connexion with the geometrical isomerism of curcumin and *isocurcumin*, there is some evidence that *cinnamylidenemesityl oxide* and *piperonylidene-mesityl oxide* exist in two forms.

Most of the compounds examined in the course of this investigation are fluorescent. They are arranged in the following list in the order of their intensity of fluorescence:

Substances arranged in gradually diminishing order of fluorescence.	Solvent in which the greatest intensity is observed.
Curcumin ... ..	Chloroform.
Benzylidenecurcumin, CHPh:C(CO·CH:CH·C <sub>6</sub> H <sub>5</sub> [OMe]·OH) <sub>2</sub>	Acetone.
<i>p</i> -Hydroxybenzylidenemesityl oxide, OH·C <sub>6</sub> H <sub>4</sub> :CH:CH·CO·CH:CM <sub>2</sub>	Toluene
<i>o</i> -Hydroxybenzylidenemesityl oxide .....	Toluene.
Dicarbethoxycurcumin, CH <sub>2</sub> (CO·CH:CH·C <sub>6</sub> H <sub>5</sub> [OMe]·O·CO <sub>2</sub> Et) <sub>2</sub>	Acetone.
Diacetylcurcumin, CH <sub>2</sub> (CO·CH:CH·C <sub>6</sub> H <sub>5</sub> [OMe]·OAc) <sub>2</sub>	Acetone.
Divanillylidenemesityl oxide .....	Acetone.
Monobromocurcumin, CHBr(CO·CH:CH·C <sub>6</sub> H <sub>5</sub> [OMe]·OH) <sub>2</sub>	Acetone.
Monobromodicarbethoxycurcumin tetrabromide, CHBr(CO·CHBr·CHBr·C <sub>6</sub> H <sub>5</sub> [OMe]·O·CO <sub>2</sub> Et) <sub>2</sub>	Chloroform.
Dibromodicarbethoxycurcumin tetrabromide, CBr <sub>2</sub> (CO·CHBr·CHBr·C <sub>6</sub> H <sub>5</sub> [OMe]·O·CO <sub>2</sub> Et) <sub>2</sub>	Chloroform.

From these observations, it may be inferred that (1) auxochromic groups, (2) the labile hydrogen atoms, (3) the double bonds, and (4) the symmetry of the molecule increase fluorescence, but are not the invariable factors of fluorescence.

#### EXPERIMENTAL.

*Benzylidenecurcumin*, C<sub>6</sub>H<sub>5</sub>:CH:C<sub>21</sub>H<sub>18</sub>O<sub>6</sub>.—A current of dry hydrogen chloride was passed through a mixture of benzaldehyde (0·5 gram), curcumin (1·8 gram), and alcohol (40 c.c.) cooled with ice. The colour became dark violet, probably owing to the formation of curcumin hydrochloride, and in about a day the whole of the curcumin dissolved and the colour changed to orange-red. After forty-eight hours, the mixture was poured into ice-cold water, when a greenish-yellow precipitate was obtained which could not be crystallised. It was purified by solution in acetic acid and fractional precipitation by sodium acetate (sample I), and subsequently in the same way by precipitation from an alcoholic solution by water (sample II). It is soluble in alcohol, acetic acid, acetone, or chloroform, shrinks slightly at 170°, and melts at 200°:

I. 0·1060 gave 0·2695 CO<sub>2</sub> and 0·0486 H<sub>2</sub>O. C=73·5; H=5·4.

II. 0·1104 „ 0·2965 CO<sub>2</sub> „ 0·0527 H<sub>2</sub>O. C=73·25; H=5·3.

C<sub>23</sub>H<sub>24</sub>O<sub>6</sub> requires C=73·68; H=5·26 per cent.

*Condensation Product of Curcumin and Nitrosodimethylaniline*, N(CH<sub>3</sub>)<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·N:C<sub>21</sub>H<sub>18</sub>O<sub>6</sub>.—One part of curcumin and one part of nitrosodimethylaniline were dissolved in alcohol, two parts of zinc

chloride were added, and the mixture was warmed for a few minutes on the water-bath. When the colour became brown, the product was precipitated by water. A good deal of tarry matter was dissolved by treatment with 30 per cent. acetic acid. The residue could not be crystallised, but was purified by fractional precipitation from acetic acid solution by water. The substance obtained in this way is fairly readily soluble in alcohol, acetic acid, or acetone, shrinks at  $98^{\circ}$ , and melts and decomposes at  $144-145^{\circ}$ . Two fractions obtained by precipitation with water from acetic acid solution had the same melting point, and gave the following results on analysis:

- I. 0.1502 gave 7.6 c.c.  $N_2$  at  $30^{\circ}$  and 760 mm.  $N=5.7$ .  
 II. 0.1430 „ 7.1 c.c.  $N_2$  „  $29^{\circ}$  „ 758 mm.  $N=5.61$ .  
 $C_{29}H_{28}O_6N_2$  requires  $N=5.8$  per cent.

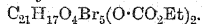
*Monobromocurcumin*,  $C_{21}H_{19}O_6Br$ .—Half a gram of curcumin was dissolved in 35 c.c. of warm chloroform, the solution cooled until curcumin began to separate, and 4.5 c.c. of a 5 per cent. solution of bromine in chloroform were then gradually added, avoiding rise of temperature. The solution became quite clear on the first addition of the bromine solution (1 c.c.), and hydrogen bromide was evolved. After ten minutes, air was blown through the mixture to drive off the chloroform, and the residual emulsion was rubbed with a little alcohol. Needle-shaped crystals of monobromocurcumin separated, which were soluble in alcohol, chloroform, acetic acid, acetone, or toluene, shrank at  $131^{\circ}$ , and melted at  $136^{\circ}$ :

- 0.1187 gave 0.0510 AgBr.  $Br=18.2$ .  
 $C_{21}H_{19}O_6Br$  requires  $Br=17.9$  per cent.

*Monobromodicarbethoxycurcumin*,  $C_{21}H_{17}O_4Br(O\cdot CO_2Et)_2$ , prepared in a similar way from dicarbethoxycurcumin, crystallises from much alcohol in needles melting at  $165-170^{\circ}$ :

- 0.1172 gave 0.0382 AgBr.  $Br=13.87$ .  
 $C_{27}H_{27}O_{10}Br$  requires  $Br=13.47$  per cent.

*Monobromodicarbethoxycurcumin tetrabromide*,



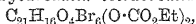
—Dicarbethoxycurcumin (1 gram) was dissolved in the minimum quantity of cold chloroform and treated with 40 c.c. of a 2.5 per cent. solution of bromine in the same solvent. After remaining at the ordinary temperature for one and a-half hours, the chloroform was driven off by a current of air. The product was extracted successively with boiling ethyl and methyl alcohols, leaving a residue which could not be crystallised, but was purified by dissolving in chloroform and fractionally precipitating with alcohol. It is

sparingly soluble in alcohol or light petroleum, and melts and decomposes at 209—210°. Different fractions gave the same analytical results:

0.1397 gave 0.1438 AgBr. Br=43.8.

$C_{27}H_{27}O_{10}Br_5$  requires Br=43.9 per cent.

*Dibromodicarbethoxycurcumin tetrabromide*,



was obtained by brominating dicarbethoxycurcumin in cold chloroform solution with excess of bromine. It separated from alcohol in colourless crystals, softening at 148° and melting at 152°. It remains unchanged on boiling with water:

0.1278 gave 0.1460 AgBr. Br=48.61.

$C_{27}H_{26}O_{10}Br_6$  requires Br=48.48 per cent.

*Monobromodiacylcurcumin*,  $C_{21}H_{17}O_4Br(OAc)_2$ .—Ciamician and Silber's diacylcurcumin was brominated in cold chloroform solution with a little more than the theoretical quantity of a chloroform solution of bromine (as in the preparation of monobromodicarbethoxycurcumin). It crystallises from alcohol in needles melting at 173—174°, and is brighter in colour than diacylcurcumin itself:

0.1162 gave 0.042 AgBr. Br=15.38.

$C_{25}H_{28}O_8Br$  requires Br=15.03 per cent.

*Dibromodiacylcurcumin tetrabromide*,  $C_{21}H_{16}O_4Br_6(OAc)_2$ , was obtained by brominating diacylcurcumin in cold chloroform solution with excess of bromine, and was crystallised from alcohol. It melts and decomposes at 80—83°:

0.1477 gave 0.1785 AgBr. Br=51.43.

$C_{25}H_{22}O_8Br_6$  requires Br=51.45 per cent.

*Monobromodimethylcurcumin*,  $C_{21}H_{17}O_4Br(OMe)_2$ , was obtained by treating dimethylcurcumin in cold chloroform solution with a little more than the theoretical quantity of bromine. It crystallises from alcohol in needles melting at 140—141°:

0.1200 gave 0.0468 AgBr. Br=16.6.

$C_{23}H_{23}O_6Br$  requires Br=16.49 per cent.

*Dibromodimethylcurcumin tetrabromide*,  $C_{21}H_{16}O_4Br_6(OMe)_2$ .—Dimethylcurcumin dissolved in chloroform was treated with excess of bromine, when hydrogen bromide was evolved, and, after half an hour, the chloroform was evaporated. This substance could not be crystallised, but was purified by precipitation from its hot alcoholic solution with water. Distinct fractions possessed the same melting point (softens at 96°, melts at 102—104°) and gave

identical analytical results. It is soluble in chloroform or acetic acid:

0.1120 gave 0.1437 AgBr.  $\text{Br}=54.6$ .

$\text{C}_{23}\text{H}_{22}\text{O}_6\text{Br}_6$  requires  $\text{Br}=54.87$  per cent.

*Conversion of Dicarbethoxycurcumin into Heller's Dicarbethoxyisocurcumin.*

A mixture of 1 gram of dicarbethoxycurcumin, 10 c.c. of acetic anhydride, and 1 c.c. of pyridine was digested at the boiling point for forty-five minutes. Alcohol (6 c.c.) and a little water were added to the cooled mixture, and the supernatant liquid was decanted from the viscous mass which thus separated. From the latter, by stirring with 2 c.c. of glacial acetic acid, a solid product was obtained, and this when crystallised from alcohol melted at  $142^\circ$ , which is identical with the melting point given by Heller for dicarbethoxyisocurcumin.

Found:  $\text{C}=63.0$ ;  $\text{H}=5.5$

$\text{C}_{27}\text{H}_{28}\text{O}_{10}$  requires  $\text{C}=63.28$ ;  $\text{H}=5.46$  per cent.

*Acetylation of Curcumin with Acetic Anhydride and Pyridine.*

Curcumin was digested with acetic anhydride and pyridine under the same conditions as described in the last paragraph, and a solid product isolated. The yellow solid obtained in this way was fractionally crystallised from acetic acid. The first fraction (which was only a minor portion) melted at  $169-170^\circ$ , and was found to be identical with Ciamician and Silber's diacetylcurcumin (mixed melting point). The second fraction (major portion) melted at  $154^\circ$ , and this, it is interesting to note, is identical with that given by Jackson for his diacetyl compound obtained by means of acetic anhydride and sodium acetate.

Found:  $\text{C}=66.4$ ;  $\text{H}=5.23$ .

$\text{C}_{25}\text{H}_{24}\text{O}_8$  requires  $\text{C}=66.37$ ;  $\text{H}=5.3$  per cent.

*Deacetylation of Diacetylcurcumin (m. p.  $154^\circ$ ) and Isolation of Heller's isoCurcumin.*

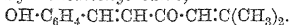
One gram of this diacetyl compound was dissolved in 15 c.c. of acetic acid, 1 c.c. of sulphuric acid (D 1.84) added, the mixture warmed for a minute, cooled, and poured into water. The yellow precipitate was dried on porous porcelain and extracted with hot benzene. The benzene solution, on cooling, deposited the substance as a yellow, amorphous powder, soluble in cold alcohol, acetic acid, acetone, ethyl acetate, or chloroform, sintering at  $140^\circ$  and melting

about 280°. There could be little doubt that this compound was identical with Heller's *isocurcumin*:

0.1130 gave 0.2822 CO<sub>2</sub> and 0.0571 H<sub>2</sub>O. C=68.1; H=5.6.

C<sub>21</sub>H<sub>20</sub>O<sub>6</sub> requires C=68.4; H=5.43 per cent.

*p-Hydroxybenzylidenemesityl oxide*,



—To an alcoholic solution of 2.4 grams of *p*-hydroxybenzaldehyde and 1 gram of mesityl oxide, 1.5 grams of zinc chloride were added, and the liquid was boiled for two hours. The solution, after concentration, was poured into water, causing the deposition of oily drops, which became crystalline on agitation. On recrystallisation from alcohol, yellow crystals were obtained, which melted at 120° and dyed yellow shades on chrome-mordanted wool:

0.1210 gave 0.3590 CO<sub>2</sub> and 0.0784 H<sub>2</sub>O. C=80.91; H=7.2.

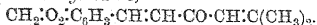
C<sub>13</sub>H<sub>14</sub>O<sub>2</sub> requires C=81.25; H=7.36 per cent.

*o-Hydroxybenzylidenemesityl oxide* was prepared in a similar way to the corresponding *p*-hydroxy-compound. The crude product separated as an oil, which was obtained crystalline by dissolving in aqueous potassium hydroxide, allowing to remain for a few days, and precipitating with hydrochloric acid. The substance dissolves with a very beautiful orange-red colour in potassium hydroxide solution:

0.1000 gave 0.2970 CO<sub>2</sub> and 0.0667 H<sub>2</sub>O. C=81.0; H=7.42.

C<sub>13</sub>H<sub>14</sub>O<sub>2</sub> requires C=81.25; H=7.36 per cent.

*Piperonylidenemesityl oxide*,



—Piperonal (2.6 grams) and mesityl oxide (2 grams) were dissolved in alcohol, and alcoholic potassium hydroxide was added to render the solution fairly alkaline. The mixture was boiled for a few minutes, when an orange-coloured substance began to separate. On cooling, this solid was collected, dissolved in acetic acid, and reprecipitated with water, when it melted at 130—135° (A). This proved to be a mixture of two substances melting at 148—153° and 175—178° respectively, which can be separated either by fractional precipitation by alcohol from acetic acid or by extraction with alcohol, in which the substance of higher melting point is scarcely soluble. The hot alcoholic extract, on cooling, deposits the substance, which melts at 148—153° (B). The insoluble residue, dissolved in chloroform and fractionally precipitated by alcohol (the first fraction being rejected), melted at 175—178° (C):

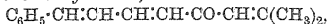
(A) 0.1000 gave 0.2662 CO<sub>2</sub> and 0.0558 H<sub>2</sub>O. C=72.6; H=6.2.

(B) 0.1150 „ 0.3040 CO<sub>2</sub> „ 0.0580 H<sub>2</sub>O. C=72.1; H=5.6.

(C) 0.1021 „ 0.2710 CO<sub>2</sub> „ 0.0533 H<sub>2</sub>O. C=72.4; H=5.8.

C<sub>14</sub>H<sub>14</sub>O<sub>3</sub> requires C=73.0; H=6.08 per cent.



*Cinnamylidenemesityl oxide,*

was prepared in the same way as the above piperonylidene compound. On cooling the reaction mixture, some viscous substance was deposited, from which the supernatant liquid was decanted and poured into water. The semi-solid mass was dissolved in acetic acid and precipitated with alcohol. It melts and decomposes at  $180-182^\circ$  ( $\alpha$ ). Addition of water to the filtrate caused the separation of a second substance, which melted and decomposed at  $88^\circ$  ( $\beta$ ). Both the  $\alpha$ - and  $\beta$ -compounds were soluble in alcohol, chloroform, acetone, or toluene, but could not be crystallised from any of these solvents. Experiment showed that these compounds were interconvertible; the former ( $\alpha$ ) on boiling with acetic acid for two to three minutes and adding water to the solution gave the  $\beta$ -compound melting at  $88^\circ$ , whereas the latter on boiling with alcohol for about five minutes gave, on cooling the solution thus obtained, a deposit of the  $\alpha$ -compound melting at  $180-182^\circ$ .

The  $\alpha$ -compound is less readily soluble in alcohol than the  $\beta$ :

( $\alpha$ ) 0.1082 gave 0.3365  $\text{CO}_2$  and 0.0670  $\text{H}_2\text{O}$ .  $\text{C}=84.4$ ;  $\text{H}=6.8$ .

( $\beta$ ) 0.1494 „ 0.4610  $\text{CO}_2$  „ 0.0808  $\text{H}_2\text{O}$ .  $\text{C}=84.1$ ;  $\text{H}=6.0$ .

$\text{C}_{14}\text{H}_{15}\text{O}$  requires  $\text{C}=84.4$ ;  $\text{H}=6.4$  per cent.

*Divanillylidenemesityl oxide* (II, p. 293).—A current of dry hydrogen chloride was passed into an ice-cooled alcoholic solution of 2.6 grams of vanillin and 1 gram of mesityl oxide, when the liquid became deep blue. After two days, the solution was poured into cold water, the precipitate collected and triturated with sodium acetate solution. The brown, amorphous powder obtained in this way could not be crystallised, and was purified by fractional precipitation from acetic acid with water solution. It is soluble in alcohol, chloroform, or acetone, softens at  $165^\circ$ , and melts at  $178^\circ$ . Distinct fractions obtained by the above described method gave identical analytical results:

I. 0.1200 gave 0.316  $\text{CO}_2$  and 0.067  $\text{H}_2\text{O}$ .  $\text{C}=71.8$ ;  $\text{H}=6.2$ .

II. 0.1065 „ 0.282  $\text{CO}_2$  „ 0.059  $\text{H}_2\text{O}$ .  $\text{C}=72.21$ ;  $\text{H}=6.1$ .

$\text{C}_{22}\text{H}_{22}\text{O}_5$  requires  $\text{C}=72.1$ ;  $\text{H}=6$  per cent.

I take this opportunity of thanking Prof. B. N. Das for his kind help and encouragement during the progress of the work.

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XXXI.—*The Rotatory Dispersive Power of Organic Compounds. Part IX. Simple Rotatory Dispersion in the Terpene Series.*

By THOMAS MARTIN LOWRY and HAROLD HELLING ABRAM.

IN a paper on "The Form of the Rotatory Dispersion Curves," published in 1913 (T., **103**, 1067), it was shown:

(a) That the rotatory dispersion in a large number of simple organic compounds may be expressed by the formula

$$a = k / (\lambda^2 - \lambda_0^2),$$

where  $k$  is the "rotation constant" and  $\lambda_0^2$  is the "dispersion constant" of the substance.

(b) That this formula can be applied both to magnetic and to natural rotatory powers.

(c) That a very simple method of testing the form of the dispersion curves is to plot the reciprocals of the rotatory powers against the squares of the wave-lengths. When the simple dispersion formula is valid, the observations will plot out to a straight line.

The validity of this simple dispersion formula was established in several ways. Thus:

(1) Twenty-five hydrocarbons, alcohols, and acids for which the ratio  $\alpha_{4358}/\alpha_{5461} = 1.636$  were grouped together, and their *magnetic* dispersion ratios were averaged for six different wave-lengths; these averages showed a remarkable agreement with the ratios calculated by means of the simple dispersion formula.

(2) In the same way the *optical* dispersion ratios of eight secondary alcohols, for which  $\alpha_{4358}/\alpha_{5461} = 1.651$ , were found to agree closely with ratios calculated by the simple formula.

(3) A few optical and magnetic rotations of larger magnitude showed a similar close agreement in individual cases, without the necessity for averaging which arises when the readings are small.

(4) In the case of  $\alpha$ - and  $\beta$ -methyl glucosides, very concordant results were obtained when the two constants of the simple equation were calculated (a) from the mercury readings  $\alpha_{4358}$  and  $\alpha_{5461}$ , (b) from the cadmium readings  $\alpha_{5086}$  and  $\alpha_{6438}$  (Lowry and Abram, *Trans. Faraday Soc.*, 1914, **10**, 108).

These earlier observations showed that the simple dispersion formula can be applied very generally to compounds of simple structure, such as the optically active secondary alcohols, which contain only a single asymmetric carbon atom and also to com-

pounds such as the glucosides which contain several asymmetric carbon atoms associated with the simplest possible radicles, for example, hydrogen, hydroxyl, and the like. An opportunity has, however, occurred recently of testing the validity of this same simple formula in the case of a large number of optically active compounds in which these elements of simplicity in the molecular structure are conspicuously absent. The striking results of this further test form the subject of the present communication.

The new data now under consideration were provided by the observations of Prof. Rupe, who in continuation of earlier experiments on the "Influence of Constitution on the Rotatory Power of Optically Active Substances" (*Annalen*, 1903, **327**, 157; 1909, **369**, 311; 1910, **373**, 121; 1913, **395**, 87, 136; 1913, **398**, 372; 1914, **402**, 149) has published a series of measurements of the optical rotatory power of (1) twelve derivatives of methylenecamphor, (2) menthol and eleven of its esters, (3) myrtenol and eleven of its esters, (4) three hydrocarbons derived from citronellaldehyde, (5) camphor, pulegone, and carvone (*Annalen*, 1915, **409**, 327). Unlike the previous series of measurements, which were confined to observations with sodium light, the last series included, in the case of almost every compound, readings for four different wave-lengths in the visible region of the spectrum. It was therefore possible to study, not only the optical rotatory power of the various compounds, but also the character of their rotatory dispersion.

The four wave-lengths, selected from a continuous spectrum, were  $\lambda = 6563$ , 5898, 5463, and 4861, corresponding closely with the Fraunhofer lines:  $C = 6563$ ,  $D = 5893$ ,  $F = 4861$ , and the green mercury line Hg 5461. In order to preserve a convenient sequence of lettering, these four wave-lengths were described as  $C$ ,  $D$ ,  $E$ , and  $F$ ; but, as the symbol  $E$  has long been applied to the Fraunhofer line of wave-length 5270, the symbol  $Q$  is used below for the green (quicksilver) line in the series, which thus becomes  $C$ ,  $D$ ,  $Q$ ,  $F$ .

The various substances were examined either in the pure state as liquids at  $20^\circ$  or dissolved in benzene at  $20^\circ$ , since this solvent was found to have no very great influence on the rotatory powers; several substances were examined both in the pure state and in solution.

When the experimental work was approaching completion, the data were handed over for detailed analysis to Dr. A. Hagenbach, Professor of Physics in the University of Basle. The important deductions which he was able to make are set out in a paper on "Rotatory Dispersion in Homologous Series" (*Zeitsch. physikal.*

*Chem.*, 1915, **89**, 570). The chief points of this paper are as follows:

(1) The dispersion ratio  $\alpha_F/\alpha_C$  is practically constant in each series of closely-related compounds. Compounds which differ in any marked degree from the average are regarded as "relatively anomalous."

(2) A similar statement may be made in reference to all the six ratios  $\alpha_F/\alpha_C$ ,  $\alpha_F/\alpha_D$ ,  $\alpha_F/\alpha_G$ ,  $\alpha_G/\alpha_C$ ,  $\alpha_G/\alpha_D$ ,  $\alpha_D/\alpha_C$ , as was shown by tabulating these ratios for (i) eight derivatives of methylenecamphor, (ii) menthol and seven of its esters, (iii) three hydrocarbons from citronellaldehyde.

(3) It follows, therefore, that if the dispersion law for one member of the series be given by the equation  $\alpha = \phi(\lambda)$ , the rotatory dispersion in every compound may be expressed by equations, such as:

$$[\alpha_1] = C_1 \phi(\lambda).$$

$$[\alpha_2] = C_2 \phi(\lambda).$$

$$[\alpha_3] = C_3 \phi(\lambda).$$

This proportionality of rotatory powers was demonstrated by tabulating the ratios  $\alpha_2/\alpha_1$ ,  $\alpha_3/\alpha_1$ ,  $\alpha_4/\alpha_1$ , etc., in each of the three series of compounds.

Attempts were made to determine, mainly by graphical methods, the nature of the unknown function  $\phi(\lambda)$ . Thus, the equations of Biot,

$$\alpha = B/\lambda^2,$$

and of Stefan,

$$\alpha = A + B/\lambda^2,$$

were tested by plotting  $\alpha$  against  $1/\lambda^2$ . Boltzmann's equation:

$$\alpha = A/\lambda^2 + B/\lambda^4 \quad \text{or} \quad \alpha\lambda^2 = A + B/\lambda^2,$$

was tested by plotting  $\alpha\lambda^2$  against  $1/\lambda^2$ . In neither case was an exact linear law disclosed. The equations of Lommel, and the two-term equation which Drude used to express the rotatory power of quartz, could not be tested in this way; but the empirical equations:

$$\alpha = A + B/\lambda^n \quad \text{and} \quad \log \alpha = A + B/\lambda$$

were tested by plotting  $\log \alpha$  against  $\log 1/\lambda$  and against  $1/\lambda$ ; subsequently,  $\log \alpha$  was also plotted against  $\lambda$ , and  $\alpha$  against  $1/\lambda$  (*Annalen*, 1915, **409**, 349, 351), but again without disclosing any simple linear relation between these quantities. The nature of the function in the equation  $\alpha = \phi(\lambda)$  thus remained still undiscovered. The present paper serves to supply this deficiency by showing that in almost every case the new dispersion data can be

expressed by a simple equation of the type first put forward by Drude.

The fact that Drude's equation was not used by Hagenbach, and in general failed during many years to secure the practical recognition which it deserves, may be accounted for in two ways. In the first place the equation was put forward, as an approximation only, in a very general form:

$$\alpha = \sum \frac{k_n}{\lambda^2 - \lambda_n^2},$$

containing an indefinite number of arbitrary constants. The arbitrary constants,  $\lambda_1^2$ ,  $\lambda_2^2$ ,  $\lambda_3^2$ , . . . , in the denominator were deduced from measurements of refractive dispersion, and it was not even suggested that they could be derived (in a still more satisfactory way and often with much greater exactness) from the rotations themselves. In the second place, Drude demonstrated the validity of his equation only in one single case, namely, that of quartz, the equation for which took the form

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1^2} - \frac{k}{\lambda^2}.$$

No data whatever were given for optically active liquids, and the magnetic rotatory dispersion in carbon disulphide and in creosote (!) was expressed by a different formula, also depending on measurements of refractive dispersion. The first extensive practical application of Drude's formula was therefore made less than six years ago in the second paper of the present series.

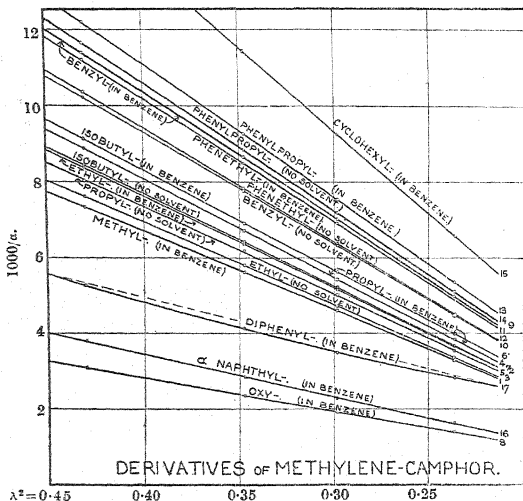
The easiest (although perhaps the least exact) method of testing the simple dispersion law,  $\alpha = k/(\lambda^2 - \lambda_0^2)$ , is to plot the reciprocals of the rotations against the squares of the wave-lengths. The dramatic effects which are produced by plotting  $1/\alpha$  against  $\lambda^2$  are shown by comparing the straight lines of Figs. 1 to 4 with the broken lines\* or curves which were given by all other methods of plotting. It is specially remarkable that plotting  $\alpha$  against  $1/\lambda^2$  (Stefan's formula) should give curves, where plotting  $1/\alpha$  against  $\lambda^2$  (Drude's formula) gives very exact straight lines. These lines indicate clearly that, where half a dozen other relationships have failed, the simple Drude formula gives at once a satisfactory expression of the experimental data.†

\* Hagenbach appears to have plotted his curves on the assumption that the "E" line used by Rupe was the Fraunhofer line  $\epsilon_{5270}$ , and not the mercury line  $\epsilon_{5461}$ .

† More exact data may perhaps compel the use of additional terms, as in the case of quartz, which requires one, two, or three terms, according to the range and accuracy of the data employed, but there are no indications of this in the data examined hitherto.

A marked exception occurs in the case of pulegone, which gives a smooth, full curve, and evidently shows "complex" rotatory dispersion. Diphenylmethylenecamphor,  $C_{10}H_{14}O:CPh_2$ , the dispersion ratios of which are much lower than those of all the related compounds, gives a curve; so also does menthyl  $\beta$ -phenylcinnamate,  $C_{10}H_{19}O \cdot CO \cdot CH:CPh_2$ , the rotatory dispersion of which must be complex, since the dispersion ratio,  $\alpha_F/\alpha_C = 1.72$ , falls below the

FIG. 1.



Rotatory dispersion in derivatives of methylenecamphor.

Notice curvature in the case of the diphenyl derivative.

minimum value  $\alpha_F/\alpha_C = \lambda_C^2/\lambda_F^2 = 1.818$ , beyond which  $\lambda_0^2$  would become negative and  $\lambda_0$  an imaginary quantity; the fact that both these compounds contain the group  $:CPh_2$  can at present only be regarded as a coincidence. All the other compounds appear, as a result of this rough graphical analysis over a narrow range of wave-lengths, to give simple rotatory dispersion.

A more exact test of the dispersion formula is given by numerical calculation. The following table shows that the specific rotations,

observed and calculated, of a series of typical compounds lie well within the range of possible experimental errors.

TABLE I.

*Specific Rotations, Observed and Calculated.*

Ethylidenecamphor,\*  $[\alpha] = 47.322/(\lambda^2 - 0.0829)$ .

Obs. ....	136.37°	178.58°	219.31°	308.49°
Calc. ....	136.05	178.58	219.55	308.49
O—C .....	+0.32	±	-0.24	±

Hydroxymethylenecamphor,\*  $[\alpha] = 22.843/(\lambda^2 - 0.0874)$ .

Obs. ....	66.53	87.66	108.57	153.41
Calc. ....	66.53	87.70	108.26	153.41
O—C .....	±	-0.06	+0.33	±

Benzylmethylenecamphor,  $[\alpha] = 33.431/(\lambda^2 - 0.0887)$ .

Obs. ....	97.87	129.00	156.26	226.50
Calc. ....	97.75	129.00	156.39	226.50
O—C .....	+0.12	±	-0.13	±

Menthol,\*  $[\alpha] = 15.068/(\lambda^2 - 0.0236)$ .

Obs. ....	37.01	46.58	54.78	70.84
Calc. ....	37.01	46.47	54.82	70.84
O—C .....	±	+0.11	-0.04	±

Menthyl benzoate,\*  $[\alpha] = 29.364/(\lambda^2 - 0.0255)$ .

Obs. ....	72.41	91.10	107.76	139.30
Calc. ....	72.46	91.10	107.59	139.30
O—C .....	-0.05	±	+0.17	±

Myrtenol,  $[\alpha] = 14.700/(\lambda^2 - 0.0316)$ .

Obs. ....	36.83	46.49	55.04	71.81
Calc. ....	36.83	46.48	55.09	71.81
O—C .....	±	+0.01	-0.05	±

Myrtenyl benzoate,  $\alpha = 11.505/(\lambda^2 - 0.0341)$ .

Obs. ....	29.01	36.67	43.51	56.90
Calc. ....	29.01	36.67	43.52	56.90
O—C .....	±	±	-0.01	±

\* Dissolved in benzene.

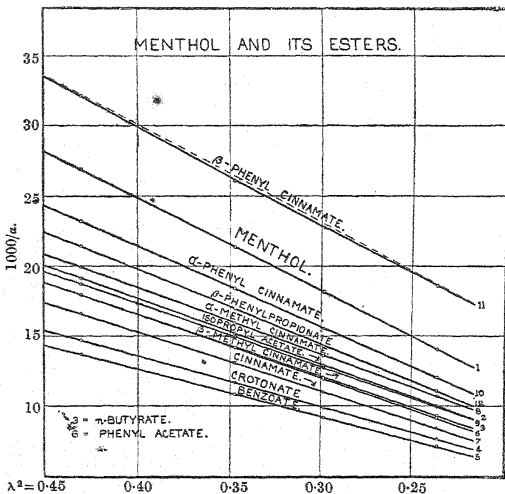
In view of the fact that the readings for solutions in benzene were multiplied by ten to convert them into specific rotations, whilst the others were approximately doubled, the agreement shown above is practically perfect.

Even clearer evidence of the validity of the simple dispersion formula is afforded by a study of the average dispersion ratios observed and calculated for groups of related compounds. Three such groups were averaged by Hagenbach, namely:

(a) Eight derivatives of methylenecamphor (dissolved in benzene),  $a_F/a_C = 2.310$ .

(b) Seven esters of menthol (pure or in benzene),  $a_F/a_C = 1.920$ .

FIG. 2.



*Rotatory dispersion in menthol and its esters.*

Notice curvature in the case of  $\beta$ -phenylcinnamate.

(c) Three derivatives of citronellaldehyde (in the pure state),  $a_F/a_C = 1.991$ .

To these there are now added average ratios for:

(d) Six derivatives of methylenecamphor (in the pure state),  $a_F/a_C = 2.303$ .

(e) Menthol and seven esters (dissolved in benzene),  $a_F/a_C = 1.911$ .



(f) Myrtenol and eight esters (in the pure state),  $\alpha_F/\alpha_C = 1.958$ . The close agreement between the observed and calculated values of these ratios is shown in table II.

FIG. 3.

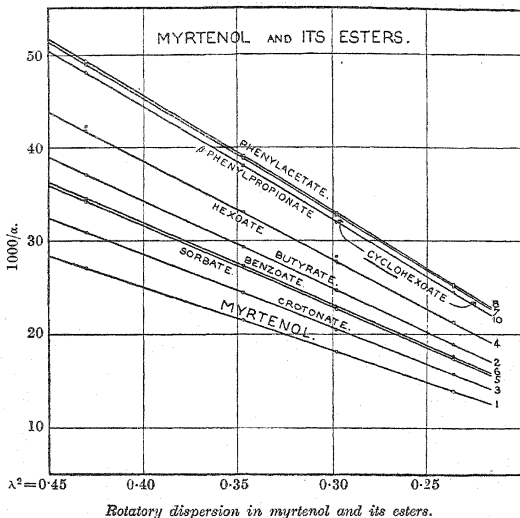


TABLE II.

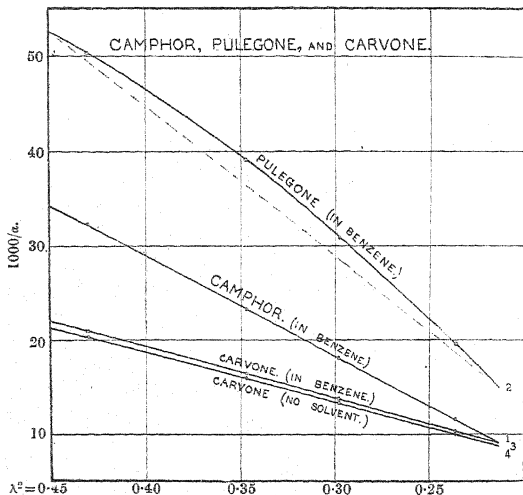
*Dispersion Ratios, Observed and Calculated.*

		$\alpha_F/\alpha_C$	$\alpha_F/\alpha_D$	$\alpha_F/\alpha_Q$	$\alpha_Q/\alpha_C$	$\alpha_Q/\alpha_D$	$\alpha_D/\alpha_C$	
(a)	{ Obs. ....	2.310	1.751	1.415	1.633	1.237	1.319	$\lambda_0^2 =$
	{ Calc. ...	2.310	1.752	1.418	1.629	1.236	1.318	0.0879
(b)	{ Obs. ....	1.920	1.529	1.294	1.488	1.181	1.259	$\lambda_0^2 =$
	{ Calc. ...	1.921	1.529	1.294	1.484	1.181	1.257	0.0250
(c)	{ Obs. ....	1.991	1.561	1.313	1.515	1.188	1.274	$\lambda_0^2 =$
	{ Calc. ...	1.992	1.569	1.316	1.513	1.191	1.269	0.0401
(d)	{ Obs. ....	2.303	1.756	1.423	1.619	1.234	1.312	$\lambda_0^2 =$
	{ Calc. ...	2.303	1.748	1.417	1.626	1.234	1.318	0.0871
(e)	{ Obs. ....	1.911	1.521	1.289	1.482	1.180	1.256	$\lambda_0^2 =$
	{ Calc. ...	1.911	1.522	1.292	1.479	1.179	1.255	0.0227
(f)	{ Obs. ....	1.958	1.550	1.306	1.499	1.186	1.264	$\lambda_0^2 =$
	{ Calc. ...	1.958	1.550	1.306	1.499	1.186	1.264	0.0334

This agreement is nearly as close as in the case of the data by which the validity of the simple Drude formula was first established, and even the largest differences are usually less than the average errors of the individual ratios. The "simple" character of the rotatory dispersion could therefore only be called in question if data were available of greater exactness or over a wider region of the spectrum.

A further opportunity of testing the validity of the simple dis-

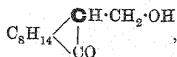
FIG. 4.



Rotatory dispersion in derivatives of camphor pulegone and carvone.

Notice curvature in the case of pulegone.

persion law is provided by the inclusion in a more recent paper by Prof. Rupe (*Helv. Chim. Acta*, 1918, **1**, 452) of dispersion data for four samples of camphylcarbinol,



a compound containing three asymmetric carbon atoms as com-

ponents of a complex ring system. The agreement between the observed and calculated rotations is shown in table III.

TABLE III.

*Rotatory Dispersion in Camphylcarbinol.*

First sample,  $[\alpha] = 15.980/(\lambda^2 - 0.10220)$ .

	$\lambda = 6563$	5898	5463	4861
Obs. ....	48.64°	65.24°	81.57°	119.17°
Calc. ....	48.64	65.05	81.43	119.17
O-C .....	±	+0.19	+0.14	±

Second sample,  $[\alpha] = 15.213/(\lambda^2 - 0.10223)$ .

Obs. ....	46.31	62.11	77.67	113.48
Calc. ....	46.31	61.93	77.53	113.48
O-C .....	±	+0.18	+0.14	±

Third sample,  $[\alpha] = 15.252/(\lambda^2 - 0.10239)$ .

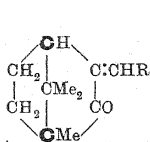
Obs. ....	46.45	62.22	77.74	113.90
Calc. ....	46.45	62.13	77.79	113.90
O-C .....	±	+0.09	-0.05	±

Fourth sample,  $[\alpha] = 16.10/(\lambda^2 - 0.10304)$ .

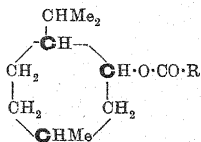
Obs. ....	49.13	65.73	82.44	120.82
Calc. ....	49.13	65.76	82.39	120.82
O-C .....	±	-0.03	+0.05	±

It will be observed that the sample having the highest rotatory power, which was also probably the purest, gives a remarkably close agreement, the differences being in opposite directions and amounting only to a few hundredths of a degree, or about 1 part in 2000. This exact agreement suggests that the simple dispersion law may be of value as a test of purity, and that deviations from it may in some cases justify a further examination of the chemical composition of the material used for the measurements.

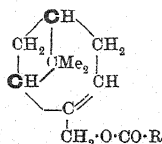
It is of interest to notice the chemical character of the compounds to which the "simple" dispersion formula has now been applied. They are as follows:



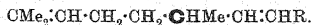
1. Methylene camphors.



2. Menthol esters.



3. Myrtenol esters.



4. Hydrocarbons from citronellaldehyde.

Nearly all are complex ring compounds or loaded with double bonds. The fact that the simple formula applies to compounds of such complex structure is remarkable evidence of the broad and sound basis on which the formula rests.

*Characteristic Wave-lengths.*—In Drude's simple equation, the rotatory dispersion is defined completely by the "dispersion constant"  $\lambda_0^2$ ; this is the square of a wave-length, which is that of a hypothetical absorption band, usually in the ultra-violet region of the spectrum. This wave-length defines the whole course of the dispersion curve, and is independent of the particular wave-lengths used to determine it; thus the value of  $\lambda_0^2$  may be deduced equally well from the mercury ratio  $\alpha_{4358}/\alpha_{5461}$ , from the cadmium ratio  $\alpha_{5088}/\alpha_{6438}$ , or from the ratio  $\alpha_F/\alpha_C$  derived from the data now under discussion. A preliminary study of these data by Prof. Rupe had, however, disclosed the fact that, in the case of the methylene-camphors,  $\alpha_F/\alpha_C = \alpha_D$ , whilst in the case of the citronellaldehyde hydrocarbons,  $\alpha_F - \alpha_C = \alpha_D$ , that is, for each series there is a "characteristic wave-length,"  $\lambda_a$  (*Zeitsch. physikal. Chem.*, 1915, **89**, 581), for which the rotation is equal to the difference between the rotations for the *F* and *C* lines. This wave-length is not a fundamental constant of the dispersion curve like the  $\lambda_0^2$  of Drude's equation, since it depends on the two standard wave-lengths, for example, *F* and *C*, which are selected as determining the difference; but it usually lies within the limits of the visible spectrum and affords a picturesque method of setting out the essential features of the dispersion curve. By assuming the validity of Stefan's formula, Hagenbach showed that this wave-length can be deduced from the expression

$$\frac{1}{\lambda_a^2} = \frac{\alpha_C}{\alpha_F - \alpha_C} \left\{ \frac{1}{\lambda_F^2} - \frac{1}{\lambda_C^2} \right\} - \frac{1}{\lambda_C^2},$$

or, taking in all the four rotatory powers,

$$\frac{1}{\lambda_a^2} = \frac{\alpha_F - \alpha_C - \alpha_D}{\alpha_C - \alpha_D} \left\{ \frac{1}{\lambda_C^2} - \frac{1}{\lambda_D^2} \right\} - \frac{1}{\lambda_D^2}.$$

Drude's equation, on the other hand, which is the one that actually fits the curves, gives for the "characteristic wave-length" the expression

$$\lambda_a^2 = \frac{\lambda_C^2 - (n-2)\lambda_F^2}{(n-1)^2} = \frac{0.4307 - 0.2363(n-2)}{(n-1)^2},$$

where  $n$  is the dispersion ratio  $\alpha_F/\alpha_C$ . Thus, for the citronellaldehyde hydrocarbons, for which  $n=2.00$ , this equation gives  $\lambda_a^2 = \lambda_C^2$ , as was observed experimentally when it was found that  $\alpha_F - \alpha_C = \alpha_D$ .

*Constant Rotatory Dispersion in Homologous Series.*—In the compounds now under consideration, new radicles are introduced into the molecule at points which are separated from the asymmetric carbon atoms by a considerable chain, including in every case either an oxygen atom or a double bond. A constant dispersion ratio is therefore observed from the beginning, and any substance of which the rotatory dispersion differs largely from the average of the series is noteworthy and exceptional. The only conspicuous exceptions amongst some thirty-six compounds under consideration in the present research were found in two substances containing the group  $\text{:CPh}_2$ . These have now been shown to differ from the others also in giving complex instead of simple dispersion curves, so that the rule appears to apply without exception to all compounds showing simple rotatory dispersion.

A different state of affairs prevails, however, in the secondary alcohols of Pickard and Kenyon, which have a "growing chain" attached directly to the asymmetric carbon atom. The dispersion is here always simple, but the dispersion constant varies in the different series, and only assumes a steady value in each series when the "growing chain" of carbon atoms has definitely established itself as the heaviest radicle attached to the asymmetric carbon atom (Lowry, Pickard, and Kenyon, T., 1914, 105, 101). The lowest homologues usually show an exceptionally high rotatory dispersion, but this is not accompanied by any change in the type of the dispersion curve, and is therefore entirely distinct from the "anomalous rotatory dispersion," of which an exact definition was given in a former paper of the present series (T., 1915, 107, 1195). It would be a real misfortune if substances which are perfectly normal in their rotatory dispersion were to be regarded even as "relatively anomalous" whenever they happen to differ slightly from their homologues, and it is hoped that this unnecessary and misleading description will be abandoned.

#### *Summary.*

It is shown that the simple dispersion formula

$$\alpha = k/(\lambda^2 - \lambda_0^2)$$

can be applied to express the rotations produced by a large number of compounds of the terpene series, including (a) derivatives of methylenecamphor, including camphylcarbinol, (b) menthol and its esters, (c) myrtenol and its esters, and (d) hydrocarbons derived from citronellaldehyde. Pulegone, and two compounds containing the group  $\text{:CPh}_2$ , show complex rotatory dispersion.

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XXXII.—*A New Sector Spectrophotometer.*

By SAMUEL JUDD LEWIS.

IN a paper by the author on "The ultra-violet absorption spectra of blood sera" (*Proc. Roy. Soc.*, 1917, [B], 89, 327), it was stated that the work described had been done with two sector spectrophotometers, that these were not adequate to the exacting nature of the investigation, although they were the best and most modern instruments available, and that a new photometer to the author's design was under construction. That apparatus has now been in use for several months, and the purpose of this paper is to describe it. A short account of the method of using such instruments is given in the reference mentioned above.

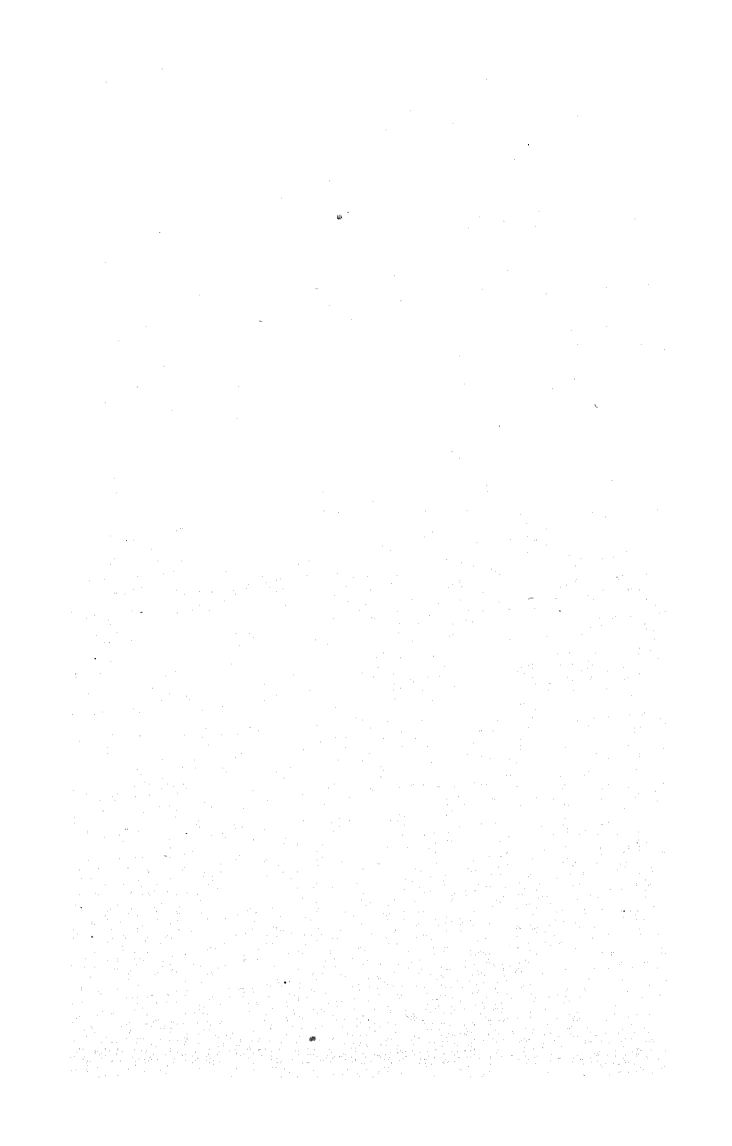
As was the case with the work detailed in the paper cited, the present development of the sector spectrophotometer has been generously supported by the Beit Research Fund Committee, the trustees of a fund which has been placed at the disposal of the British Homeopathic Association by Mr. Otto Beit for purposes of scientific research.

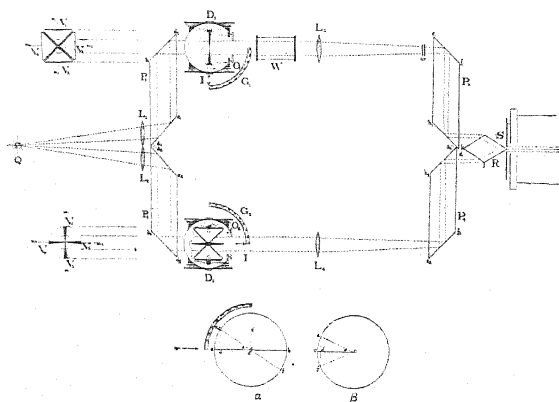
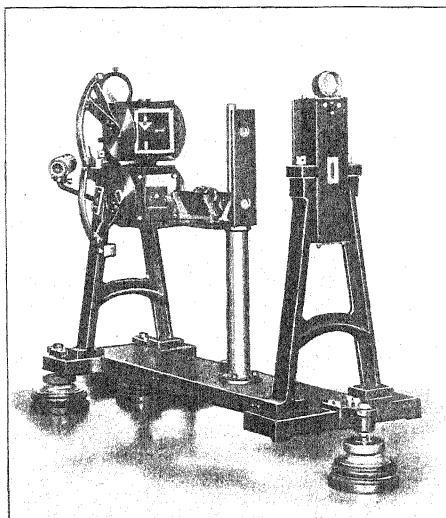
The new instrument was designed by the author in 1915 with a view to meeting the requirements of the work on blood serum. No instrument can be unnecessarily refined for this, and should it be desired to employ the method of ultra-violet absorption spectrography for clinical purposes, whether for blood serum or for any other substances, an instrument which is at once trustworthy and easy to manipulate is essential. Incidentally, an instrument which fulfils these conditions should satisfy most of the demands of scientific research and bring the practice of ultra-violet absorption spectroscopy within the range of applied chemistry. Unless or until the ideals set out are attained, absorption spectroscopy can have little more than academic significance; but perfect, easily adjustable spectrophotometers may be expected in course of time to occupy a place in the general laboratory not less important than that filled by the polarimeter or the refractometer.

Among the objects aimed at in the new design were the following:

(a) The utmost accuracy and refinement in the resulting spectra, because for the serum work it is required to discover with certainty very small differences of detail in the absorption curve, as explained in the paper cited.

(b) To work quickly as well as accurately, since it is necessary to undertake the examination of a serum at very short notice, and there is no reasonable opportunity of revising the observation, as





: [To face page 313.



the serum will usually have changed in character by the time the absorption curve is drawn; this presumes quick and perfect adjustment of the instruments.

(c) To maintain this excellent adjustment throughout an experiment, or to restore it from time to time during the progress of an observation, without the necessity of other disturbances.

(d) Precise quantitative values for the extinction coefficients, since the amplitude of the curve has important significance.

(e) To attain this high standard, and yet to be able to use the one spectrograph alternately with the photometer and for other purposes as circumstances may require.

The photograph exhibits the general appearance of the new photometer; it exposes the vanes in the upper sector, the front of the sector box having been removed; also only one platform bearing a tube carrier is shown. The arrangement of parts is displayed in the diagram.

$Q$  represents a suitable lamp, light from which falls on the two lenses  $L_1$ ,  $L_2$ , which render the light parallel. These pencils of light pass through the face  $a_1b_1$  in the reflecting prism  $P_1$  and through the face  $a_2b_2$  in the reflecting prism  $P_2$  in the manner shown, and are reflected approximately at right angles by the inclined faces  $a_1c_1$  in prism  $P_1$  and  $a_2c_2$  in the prism  $P_2$ , so that in each case the light follows a course parallel to the main axis of the prism to a second inclined face  $b_1d_1$  in prism  $P_1$  and  $b_2d_2$  in prism  $P_2$ , where it is reflected again at right angles.

The parallel beam reflected from  $b_1d_1$  passes through the sector  $D_1$ , the diaphragm  $O_1$ , and the lens  $L_3$  to the inclined face  $e_1f_1$  in reflecting prism  $P_3$ , where it is reflected at right angles along the main axis of the prism on to the inclined face  $g_1h_1$ , where it is again reflected at right angles and passes out of the prism on to the face  $ki$  of the rhomb  $R$  placed in front of the slit  $S$  of the spectrograph, or, in the absence of the rhomb, directly on to the slit.

The pencil from  $b_2d_2$  undergoes similar treatment, and eventually passes out of the photometer on to the face  $kj$  of the rhomb.

The rhomb may be dispensed with if the pencils of light are directed so as to fill the angles of the prisms at  $g_1$  and  $g_2$ , provided that one prism slightly overlaps the other, as shown in the figure, so that the prominent edge may define the line of juxtaposition. It will be seen that any stray parts of the pencils of light would be reflected or escape out of the field.

The essential part between the two prisms in either path is the sector  $D_1$ ,  $D_2$ , capable of cutting off any desired portion of the light passing along that path.

It should be observed that the prisms and sectors are enclosed in dust-proof metal boxes provided with quartz windows.

The sector system is placed in a part of the path where the light is parallel. It consists of four vanes,  $V_1, V_2, V_3, V_4$ , as shown in the side elevations in the figure. Each vane has two edges at right angles, and when the four vanes are disposed to one another in one plane, so that the four angles meet at a point, the system is closed and no light can pass. This arrangement is represented in the upper path in the figure. The common point of the four angles is on the optic axis, to which the plane is at right angles. Each vane can be turned by means of suitable mechanism about its bisectors,  $m_1, m_2, m_3, m_4$ . When all the vanes are turned simultaneously through an angle of  $90^\circ$  about their respective bisectors, light can pass in the direction of the optic axis without any interruption except that caused by the slight obstruction due to the thickness of the material of the vanes, as shown in the figure for the lower path. By turning the vanes through any other given angle about their bisectors, a known proportion of the light may be allowed to pass. Each of the four vanes is carried on a wheel, by means of a spindle which coincides with the bisector of the vane and also forms the axle of the wheel. These wheels are mounted on the outside of the walls of the box enclosing the sector at right angles to one another, and fit into one another by bevelled cogs. They move simultaneously, and the fitting is so close that back-lash is reduced to an insignificant minimum. The amount of rotation of the vanes is measured by a pointer,  $I$ , mounted on the front wheel and moved against an arc graduated in half degrees from 0 to 90.

A diaphragm or stop,  $O_1, O_2$ , is placed in front of each sector to reduce the section of the beam of light to suitable dimensions, say 9 mm. in diameter when the observation tubes or cells have a lumen of 12 mm.

In order to correct the error caused by the obstruction due to the thickness of the material of the vanes, their edges are reduced to knife edges, and the thickness along the bisector is graduated from the minimum at its extremity at the optic axis to what is necessary, say 1 mm., at a distance of 10 mm. The two sides of each vane are equally made, and each of the four surfaces is plane or concave. Hence a section through a vane at right angles to its bisector has the form of a rhombus having two very obtuse and two very acute angles; also a section which includes the bisector has the form of an isosceles triangle.

It follows that when the sector system is open, as shown in the lower path in the figure, the obstruction or shadow produced by

each vane has the form of a geometrical sector of known dimensions, and therefore the sectional area of the pencil of light passing through the sector system is reduced by four times the area of one small sector shadow; also, each of the four apertures has the form of a geometrical sector.

Compensation for this reduction in area is made by employing for the path in which the light is to be of whole, or 100 per cent. intensity, that is, for the path in which the substance under observation is placed, a diaphragm the aperture of which is appropriately larger than that of the diaphragm in the other path. In the author's instrument, the diameter of the larger aperture is 9.3 mm. and that of the smaller 9.0 mm. These diaphragms are loose and may be used with either sector, according to whether it is desired to use the upper or lower sector.

The only limitation to this arrangement is that the sectors do not operate for those angles which are included by the small angle covered by the thickness of the vanes. In the author's instrument this is  $2.6^\circ$ , so that the range of operation is from  $2.6^\circ$  to  $90^\circ$ .

The lenses  $L_3$ ,  $L_4$ , placed between the sectors and the second set of prisms, focus the light on the slit, the focus being that for light of a wave-length of about 3000.

The edge of the rhomb is placed close to the slit, so that the two pencils of light when they emerge from either side of it into the slit may be at the focus of the collimating lens; the line of juxtaposition between the two spectra is thus very clearly defined without the least overlapping or intervening space, with the result that the lines in the two spectra, whether visual or photographic, can be compared for their relative intensities at the best advantage.

The cell containing the substance under observation is placed in the parallel beam of light between the sector and the central lens; room is provided for tubes up to 100 mm. in length, and tubes of this length were used successfully in an investigation relating to Lambert's law. As the pencil of light is 9.3 mm. in diameter, it is desirable for long tubes that the lumen of the tube should be at least 12 mm. in diameter, so as to avoid serious reflection from the inner walls of the tube. When the lumen is small and the layer of substance thin, it may be placed in the convergent beam immediately in front of the prism  $P_3$ , as shown at  $w$ , and a still smaller cell might be interposed between the prism  $P_3$  and the face  $ki$  of the rhomb, but only with due regard to existing conditions. Inasmuch as the system in the lower path of light is identical with that in the upper, the cell may be placed in the lower with equal advantage, or, as explained later, cells may be placed in both beams simultaneously.

The new instrument is characterised chiefly by its sectors; these are distinguished both in their construction and in the principles upon which they operate. In comparison and contrast with other sectors, they accommodate the whole beam of light, and not merely half, as is the case with some others; this enables exposures to be reduced to one-half in order to produce a photograph of the same intensity; the exposures being continuous, calibration of the photographic plate is avoided; the direct function of the new sectors is to cut down the intensity of the light, and not to do so indirectly by altering the exposure, as is the case with the Hilger instrument; the sector is still, which is a great convenience. The whole aperture of the sector system is made up of four sector-shaped apertures arranged diagonally about the optic axis, that is, they are disposed at an angle of  $45^\circ$  to the vertical. This has the advantage of utilising all parts of the circular beam of light in proper proportion, whatever the magnitude of the effective aperture at the moment. In this it differs from the iris and other forms of stop or sector, which reduce the intensity of the light by cutting down the light from the periphery of the beam inwards, or by cutting it down in some other way which assumes that every part of the field is equally illuminated. Under the conditions of ordinary practice, this assumption lacks sufficient justification where precise photometry is required.

The size of the sector aperture is measured in terms of the angle which it forms at the optic axis. The angle  $45^\circ$  represents an aperture of 100 per cent., and the angle formed at the optic axis by the shadow cast by one half of a vane in any given position is  $\phi$ . Hence the sector aperture is proportional to  $45^\circ - \phi$ . This method of measuring the size of the aperture is exceedingly convenient both for simplicity of calculation from the angle  $\theta$ , which is read on the graduated arc, and for the fact that apertures of any odd value may be produced at will. This will become evident from the following explanation of the manner of calculation.

When the vane  $acb$  in the figure ( $\alpha$ ) (front elevation) is turned through an angle  $\theta$ , as measured by the graduated arc, so as to take up the position  $ecf$ , each half of the vane  $ec$  or  $cf$  creates a sector-shaped shadow in a beam of light in the direction of the arrow;  $e'd'$  is a projection of  $ed$ . It is shown again in the figure ( $\beta$ ) in side elevation, where  $e'd'$  is the projection of  $ed$ . If the beam of light were rectangular in section, the shadow would be triangular in shape ( $e'd'o$ ) and proportional in area to  $\sin \theta$ , since  $ed$ , which subtends the angle  $\theta$ , is equal to  $e_1d_1$ , which subtends the angle  $\phi$  at the optic axis,  $O$ , for  $ed'$  and  $d'o$  are equal, since they form the right angle in the isosceles triangle  $ed'o$ ; therefore  $ed/ed' =$

$e'd'/d'o$ , that is,  $\sin \theta = \tan \phi$ , whence  $\theta$  being known,  $\phi$  may be found directly from the tables.

The beam of light, however, is circular in section; hence the area of any sector in the circle is proportional to the angle which it contains, that is, to  $\phi$  for the shadow and  $45^\circ - \phi$  for the sector aperture.

Only one-eighth of the whole circular aperture has been considered, but it will be seen on cancelling common factors that the whole aperture at any moment is measured by  $45^\circ - \phi$ , where  $45^\circ$  is taken to represent the fully open sector. It is convenient to express the apertures as percentages of the whole aperture, that is, as  $\frac{(45 - \phi)100}{45}$ . The percentage apertures and values for  $\log I/I'$

corresponding with each half-degree on the graduated arc have been calculated by Miss Gartha Thompson, to whom the author is indebted for valuable assistance throughout the inquiry. Examples are given in the following table:

$\theta$ .	Sin $\theta$ or tan $\phi$ .	$\phi$ .	$45 - \phi$ .	Sector aperture, per cent. $\frac{(45 - \phi) 100}{45}$	Log $I/I'$ , $\log \frac{45}{45 - \phi}$ .
				45	
10	0.1736482	9.85108	35.14892	78.11	0.1073
25	0.4226183	22.90981	22.09019	49.08	0.3091
40	0.6427876	32.73241	12.26759	27.27	0.5644
40.5	0.6494480	33.00163	11.99837	26.67	0.5740
41	0.6560590	33.27239	11.72760	26.07	0.5839
55	0.8191520	39.32269	5.67731	12.62	0.8991
70	0.9396926	43.21918	1.78082	3.958	1.4026
80	0.9848078	44.56143	0.43857	0.975	2.0111
80.5	0.9862856	44.60441	0.39559	0.870	2.0559
81	0.9876883	44.64512	0.35488	0.789	2.1031
85	0.9961947	44.89078	0.10922	0.243	2.6150
85.5	0.9969173	44.91155	0.08845	0.197	2.7065
88	0.9993908	44.98255	0.01745	0.0388	3.4114

It is evident that the values in the table can be applied to graduating the arc on the instrument so that it may read directly in terms of  $\log I/I'$ , as has been done with other instruments. This is convenient where it is intended to use the instrument for routine work only, but for versatile research, and especially where it is desired occasionally to elaborate a particular part of an absorption curve, the freedom conferred by the ordinary scale and tables will be appreciated. There is, however, no difficulty in providing both scales on the same arc.

The effect produced by the size of the shadow cast by the vane being a function of the sine of the angle through which the vane has been turned is significant. From the above figures, it will be

seen that the difference in the sector aperture produced by a constant difference of  $15^\circ$  in  $\theta$  decreases continuously, thus:

							Per cent.
Between $10^\circ$ and $25^\circ$	the aperture decreases by (78.11—49.08)						29.03
" $25^\circ$ " $40^\circ$ " " " "	" (49.08—27.27)						21.81
" $55^\circ$ " $70^\circ$ " " " "	" (12.62—3.96)						8.66
" $70^\circ$ " $85^\circ$ " " " "	" (3.96—0.24)						3.72

Again, for half-degree intervals in  $\theta$ :

Between $20^\circ$ and $20.5^\circ$	the aperture decreases by (58.03—57.09)						0.94
" $40^\circ$ " $40.5^\circ$ " " " "	" (27.27—26.67)						0.60
" $80^\circ$ " $80.5^\circ$ " " " "	" (0.975—0.879)						0.096
" $85^\circ$ " $85.5^\circ$ " " " "	" (0.243—0.197)						0.047

For any of the apertures of small size, it is evident, therefore, that a movement of the pointer on the arc over one or more divisions alters the size of the aperture by only a small fraction, so that any probable error in construction or manipulation can have no detectable effect on the measurement of the size of the aperture.

The possibility of regulating the size of the small apertures with such precision is a valuable advantage, since it is with these that much of the more important and delicate work is done.

In an investigation of uric acid, undertaken to see if it obeyed Lambert's law, it was proved that the results for all the small apertures down to 0.29 per cent. (reading  $84.5^\circ$  on the graduated arc and giving the value 2.53 for  $\log I/I'$ ) harmonised perfectly with those found for the larger apertures. The still smaller ones were not quite so true, owing to a slight imperfection in the setting of the vanes, but this can be avoided in reproducing the instrument.

The instrument is absolute in all its measurements. That it is not only so, but that it is also precise, follows from the examination of a standard piece of glass which was supplied by Messrs. Adam Hilger with their photometer for calibration purposes. The figures obtained are tabulated below. The two sets of values for  $\log I/I'$  are as follows: (a) those obtained by the new photometer; (b) the figures given by Hilger:

Wave-length.	(a).	(b).
2751	0.281	0.278
2636	0.665	0.610
2564	0.919	0.888
2478	1.318	1.330
2435	1.605	1.608
2389	1.970	1.940

Of the two methods, the one with the new photometer has the advantage of being direct and of not depending on the assumption

that photometry in the ultra-violet is uniform with that in the visible region and on the use of accessory apparatus, as in the method published by Hilger. In any case, the two series of results are sufficiently similar to one another to call for a discussion as to which is the more accurate expression of the phenomena.

Considerable advantage is gained by having two sectors which are equal in all respects, as in the new photometer. As already stated, the substance can be placed in the first and second paths alternately, so that any slight imperfections in the sectors or in any part of the optical train will express themselves in opposite senses in the two series of spectra; also the work will be confirmed and experimental error corrected at the same time. The mean of the two closely concordant results must be a very near approximation to the truth.

Further, opportunity is provided for eliminating the effect of the solvent directly. Most of the solvents, alcohol, for example, give feeble absorption spectra which spoil the accuracy of the extinction coefficients of the dissolved substance under investigation. It is not altogether satisfactory to correct the absorption constants of the solution by subtracting those due to the solvent, which have been ascertained separately, and in any case it is laborious to do so; for example, it is not safe to assume that a standard curve for absolutely pure alcohol applies to commercially pure spirit. Indeed, some of the impurities commonly occurring in rectified spirit are strongly absorbent of ultra-violet light. It is better to place in the one path a tube of the solution, and in front of the constant sector a similar tube filled with the same solvent as that used in making the solution. It is a good plan to have a tube of the given solvent in each of the two paths when adjusting the instrument, and then to replace the solvent in one of them by the solution in question. It is perhaps unnecessary to do so, but it lends a sense of satisfaction, while it adds little or nothing to the experimental work. It is certain that the differences then observed in the two spectra are due entirely to the substance in the dissolved state, and hence its absorption curve can be derived directly. There is, however, the possibility of the absorption spectrum being modified by the association of the solute with the solvent, but that is a matter for other inquiry in each particular case and does not affect either the general truth of the proposition or the operation of the instrument.

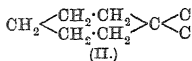
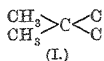
# XXXIII.—The Formation and Stability of spiro-Compounds. Part II. Bridged-spiro-compounds Derived from cycloHexane.

By CHRISTOPHER KELK INGOLD and JOCELYN FIELD THORPE.

## INTRODUCTION.

### (A) General.

IN Part I. of this series (Beesley, Ingold, and Thorpe, T., 1915, 107, 1080) a comparison was drawn between the conditions of formation and the stability of the bromo-esters of  $\beta\beta$ -dimethylglutaric acid and *cyclohexane*-1:1-diacetic acid. These two acids contain respectively the structures I and II, and the object with which



these comparisons were made may be indicated by reference to Figs. (i) and (ii), which are drawn to correspond with structures I and II. The question discussed was whether the forcing apart of the valencies (a) and (b) of a carbon atom from an inclination of  $2 \tan^{-1} \sqrt{2}$  to one of  $\frac{2}{3}\pi$  radians, which, according to Baeyer's strain theory necessarily accompanies the production of the *cyclohexane* ring, would cause the other two valencies (c) and (d) to approach one another. They might, it was suggested, approach one another in such a way as to divide the remaining space into three equal angles as in Fig. (ii A); or, alternatively, they might be quite unaffected by the straining of (a) and (b) and remain, as Fig. (ii B) shows, at the normal angle of  $2 \tan^{-1} \sqrt{2}$ .

It was pointed out that if the first of these hypotheses, that represented in Fig. (ii A), were correct, and side-chains attached to (c) and (d) were in closer proximity when (a) and (b) were bound in a *cyclohexane* ring than is the case in Fig. (i), where (a) and (b) are free, then the elimination of groups or elements such as, for example, hydrogen and bromine as hydrogen bromide, from the side-chains of substitution products of *cyclohexanedi*acetic acid should proceed with greater readiness than when corresponding derivatives of dimethylglutaric acid are employed. Further, the ring compounds formed as a result of the elimination might be expected to possess a greater general stability in the former case than in the latter. If, on the other hand, the second alternative,



for which Fig. (ii B) is drawn, is the correct one, there should be no difference in the two cases.

Experimental evidence was, as a matter of fact, clearly in favour of the first hypothesis. Thus, for example, *trans*-cyclohexanespirocyclopropane-1:2-dicarboxylic acid, which contains the carbon

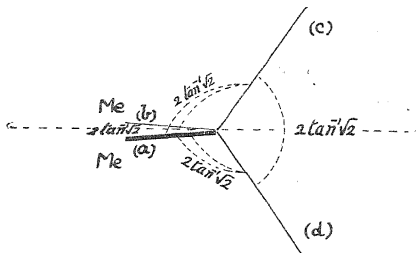


Fig. (i)

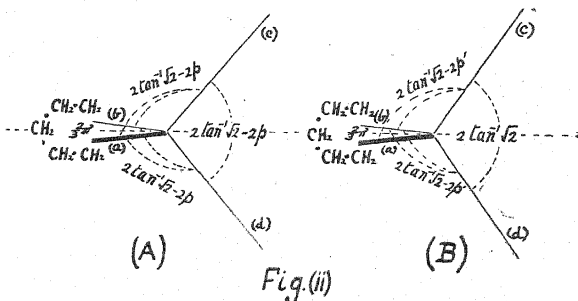
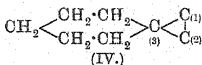
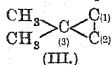


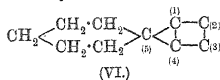
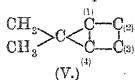
Fig. (ii)

skeleton IV, was found to possess a distinctly greater stability than *trans*-caronic acid represented by the outline III:



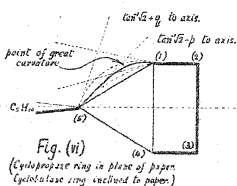
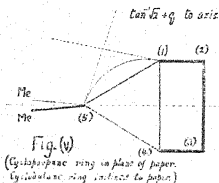
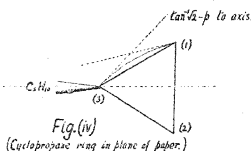
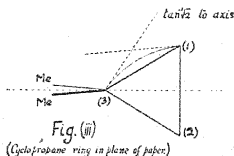
The present paper extends the comparison to substances of a rather more complex type, which contain a *cyclobutane* ring joined to the

*cyclopropane* ring by two carbon atoms common to both. The structures of these compounds are indicated by the outlines V and VI:



It is apparent that the presence of the *cyclobutane* ring in structures V and VI will make a considerable difference in the kind of effect that one might expect to observe. This can best be understood by representing the strained valencies according to a graphical method which depends for its rational basis on the following considerations.

In Fig. (iii), which is drawn to correspond with formula III, the



carbon atoms of the *cyclopropane* ring are represented as points at the corners of an equilateral triangle. Now in the case of such a compound as ethane it can scarcely be doubted that the resultant of the attracting forces which bind the two carbon atoms together, that is to say the valency, is directed along the straight line joining the centres of the carbon atoms. With *cyclopropane*, however, the case is different. For here, according to the strain theory, we have each one of the carbon atoms of the ring reacting on those of its valencies which participate in the ring in such a way as to *tend* to make them emanate from the atom in directions inclined to one another at an angle of  $2 \tan^{-1} \sqrt{2}$ . If the carbon atoms were entirely successful in bringing about this result, then, since two

valencies emanating from the same carbon atom at an angle of  $2 \tan^{-1} \sqrt{2}$  have to reach the two remaining corners of the equilateral triangle, it is clear that the only way in which they could do so is by describing curved paths. The simplest curve which, in these circumstances, a valency could describe would be the arc of a circle each of the terminal tangents of which makes an angle of  $\tan^{-1} \sqrt{2}$  with the median through the corresponding corner of the equilateral triangle. This path is drawn in the case of the valency (3:1) in Fig. (iii). It represents a state in which the carbon atoms would be entirely free from distortion of the kind we are considering, the whole being borne by the valencies; that is to say, the physical stress would reside solely on the inter-atomic medium in which the forces of valency are propagated. The valencies will, however, on their part, tend to reduce their potential energy by shortening their paths, and if they completely succeeded would stretch themselves along the straight lines joining the carbon atoms. This would throw the whole of the strain back on the latter, since now the initial directions in which the ring-valencies leave a carbon atom are inclined, not at  $2 \tan^{-1} \sqrt{2}$ , but at  $\pi/3$ . It is probable, therefore, that an equilibrium of stresses will be set up, and that the valencies will occupy paths which lie between the straight lines and the limiting arcs, the arrangement being of such a kind as to cause part of the strain to be taken up by the distorted carbon atoms and part by the bent valencies.

Experimental support can be claimed for this view. For in Part I. there were recorded experiments which yielded decided evidence that part at least of this kind of strain is actually taken up by the carbon atoms. In particular, it was shown that, when two valencies of a carbon atom are bound in a *cyclohexane* ring, groups attached to the other two valencies apparently take up an altered relative position. It is obvious that this could never happen if the strains existing in the *cyclohexane* ring resided solely on the valencies participating in the ring, none at all being borne by the carbon atom which carries the side-chains. Similarly, strains existing in one ring of a *spiro*-compound could not possibly make themselves felt in the second ring unless communicated by a spirane carbon atom, which itself is in a state of strain. According to the experiments described in Part I., such communication of strain across the spirane carbon atom appears actually to take place, and one can only conclude therefrom that the spirane atom itself is by no means in an unstrained condition.

If it be true that part at least of the strain of the *cyclohexane* ring is actually taken up by the carbon atoms, then regarding the matter from the graphical point of view, we may say that the

valencies of the *cyclohexane* ring, and presumably of any other alicyclic ring, occupy paths which are distinctly flatter than the limiting arcs the terminal tangents of which meet at the normal angle  $2 \tan^{-1} \sqrt{2}$ .

On the other hand, it will be shown in the present paper that it is more difficult to close the *cyclobutane* ring in the formation of certain bridged-*spiro*-compounds of the type VI (p. 322) than it is in the formation of corresponding bridged-ring compounds of the type V (p. 322). Further, the former, when obtained, are less stable than the latter in certain specific positions entirely in accord with the views here put forward. If the stresses existing in the *cyclohexane* ring can be communicated to the *cyclobutane* ring, or to side-chains attached to the *cyclopropane* ring before the *cyclobutane* has been closed, then it follows that the valencies of the *cyclopropane* ring, as well as the spirane carbon atom, must take part in the transmission of stress. With entirely unstrained valencies this is inconceivable, and one is therefore forced to the conclusion that the valencies themselves are strained.

The graphical aspect of this is that the valencies concerned, and therefore probably all ring-bound valencies, must occupy paths which are not straight lines, which are, in fact, distinctly curved. The curvature of such a path will, as we have already seen, be less than that of the limiting arc the terminal tangents of which meet at  $2 \tan^{-1} \sqrt{2}$ , and the path may therefore be regarded as lying somewhere between a straight line on the one hand and a limiting curve on the other.

Exactly where the position of equilibrium of a particular valency lies, and what the precise shape of its true path is, it is impossible at present to say; but the view that the true equilibrium-path lies somewhere between the rectilinear path, which represents the limiting case in which the valency is unstrained, and the curved path which stands for the other limit in which the whole of the distortion resides on the valency and none at all on the carbon atom, affords a simple, and, so far as it goes, a fairly adequate hypothesis in regard to the facts observed. If we accept the point of view that the more strained a valency is the more prone it is to break, then among the factors which determine the equilibrium of strain-distribution will certainly be found the number of groups attached to the carbon atoms concerned; for the tendency which ring compounds have to undergo fission between quaternary carbon atoms is well known. The electrochemical character of the substituents will, of course, be another determining factor.

Thus it would seem that there are three causes affecting the

stability of any valency which participates in a fully reduced alicyclic structure:

- (1) The number of carbon atoms in the ring,
- (2) The character and mode of attachment of any attached rings, and
- (3) The number, distribution, and character of the substituent groups.

In regard to the first of these causes Baeyer's simple conception has had a very great degree of success in explaining the broad facts; so much so that one cannot but accept it as an approximation to the truth. In its elemental form, however, it does not consider the question as to whether the atoms or the valencies are the seat of the postulated strain, and, consequently, is not in a position to take into account the mode of operation of causes (2) and (3), which present us with two unsolved problems. The series of which this paper is Part II. is an attack on the former of these. In regard to the latter all that can at the moment be said is that the present considerations lead to the view that whilst causes (1) and (2) determine the maximal strain or curvature which any particular valency can be called on to bear, cause (3) operates in such a way as to settle exactly what fraction of that maximum it shall bear.

The uncertainty which surrounds the operation of cause (3) constitutes a difficulty which one meets with in planning experiments with a view to study the mode of action of cause (2). If, however, one is careful only to compare substances in which similar, and similarly situated, substituent groups are present, the strain on a valency may fairly be taken to be measured by the greatest strain which that valency could be called on to bear in the limiting equilibrium. It will actually, of course, be just a fraction of this, but if the groups are alike it will be the same fraction for all the substances. In such cases, therefore, the strain existing on a valency is, from the graphical point of view, measured by the degree of curvature of the limiting curved path.

Fig. (iii), p. 322, is an application of this method to the cyclopropane ring structure III (p. 321), and has already been mentioned. The limiting curve for the valency (3:1) is drawn. Its terminal tangents make angles of  $\tan^{-1}\sqrt{2}$  with the corresponding medians, and its curvature, taking the side of the triangle as unity, is  $\sqrt{2} - \frac{1}{3}\sqrt{3}$ .

Applying the same method to the cyclohexane-spirocyclopropane structure IV (p. 321) we obtain Fig. (iv) (p. 322), in which, for reasons referred to at the beginning of this paper and given in detail in Part I., the terminal tangents of the limiting curve of the

valency (3:1) are drawn to make angles with the corresponding medians less than the normal value  $\tan^{-1}\sqrt{2}$  by, say,  $p$  radians. The curvature of this curve is less than that of the curve in Fig. (iii) by about  $\frac{1}{6}(7-2\sqrt{6})p$ , a figure which may be taken as a measure of the increase in stability of the bond (3:1) which was proved experimentally in Part I.

The structure V (p. 322) is interesting as exhibiting a difference in exactly the opposite sense. The fact that two of the valencies of the carbon atom (1) are held in a *cyclobutane* ring will, according to the views put forward in Part I., tend to make the initial directions in which the other two valencies leave the carbon atom spread out in such a way as to form angles with one another and with the *cyclobutane*-ring-bound valencies greater than would be the case if the *cyclobutane* ring had not been closed. This will involve an increase in the initial divergence of the valencies (1:4) and (1:5). The limiting arc between the carbon atoms (5) and (1) is therefore drawn (Fig. v, p. 322) to suit terminal tangents inclined to the corresponding medians at angles which are greater than  $\tan^{-1}\sqrt{2}$  by, say,  $q$  radians. The curvature is therefore greater than  $\sqrt{2}-\frac{1}{3}\sqrt{3}$  by about  $\frac{1}{6}(7-2\sqrt{6})q$ .

The point of present interest is, of course, to see how a bridged-ring compound of the type V compares with a bridged-*spiro*-compound of the type VI (p. 322). It will be observed that in the latter case the limiting curve for the valency (5:1) cannot possibly be symmetrical. For whilst the carbon atom (5) is, on account of the *cyclohexane* ring, tending to reduce the angle which the terminal direction of the curve makes with the median to the value  $\tan^{-1}\sqrt{2}-p$  radians, the carbon atom (1), as a result of its being involved in the *cyclobutane* ring, is endeavouring to enhance the corresponding angle at that end of the curve to  $\tan^{-1}\sqrt{2}+q$  radians. The true curve, therefore, will lie between the dotted arcs of curvatures  $\sqrt{2}-\frac{1}{3}\sqrt{3}-p/6(7-2\sqrt{6})$  and

$$\sqrt{2}-\frac{1}{3}\sqrt{3}+q/6(7-2\sqrt{6}),$$

approximating to the inner arc near the carbon atom (5), and to the outer near the carbon atom (1). Such a path, it is clear from Fig. (vi) (p. 322), must contain a region of comparatively great curvature, and we may therefore expect the bond (5:1) in bridged-*spiro*-compounds of the type VI (p. 322) to be noticeably less stable than the same bond in corresponding compounds of the bridged-ring series V.

The effect just noticed will, of course, be by far the greatest which the *cyclohexane* ring could be expected to have on the attached dicyclic system. The reactions on the bonds (1:2) and (1:4) will

be next in importance, but of the second order. It is, however, of interest briefly to examine them. The fact that the limiting curve of the valency (5:1) is, on the whole, depressed below the arc which corresponds with the limiting curve of the same valency in Fig. (v) necessitates that the true path of the same valency in Fig. (vi) is, even near the carbon atom (1), rather less divergent from the rectilinear path than is the case in Fig. (v). This will involve a small effect on the valency (1:2) in the direction of an increase in the curvature of its limiting curve. The bond (1:2) should therefore be slightly more strained and less stable in the series VI than in the series V.

The effect of the strains in the *cyclohexane* ring on the bridge-bond (1:4) is also of the second order, the depression of the bond (5:1) being the determining factor. In this case the fact that the bonds (1:5), (1:4), and (1:2) have their curves in different planes makes the geometrical construction more complicated. It would appear, however, that the effect should be in the direction of a decrease of stability, although, of course, a very slight one.

There remains for consideration the bond (2:3). The effect in this case will be still smaller, of the third order in fact, and probably beyond the limits of detection. It should be in the direction of an increase in stability.

It may be stated here that the results of the experiments described in this paper are in the most complete accord with all the above conclusions.

The most striking fact which emerged during the experimental study was the marked decrease in the stability of the bond (5:1), of compounds of the type VI, when compared with corresponding substances of the type V (see sections C, D, and G). The fission of this bond was brought about with great ease in certain substances of the former type by alkaline reagents which appeared to be without effect on the latter. This is in agreement with the first of the main conclusions reached as a result of the conception of flexible valencies. The agreement is particularly interesting in this case, for whereas in the comparison of the *cyclopropane* derivatives of types III and IV (p. 321) carried out in Part I. it was found, in agreement with the requirements of theory, that the *cyclohexane* ring had a stabilising influence, in the bridged series V and VI the hypothesis leads us to anticipate exactly the reverse.

Definite experimental evidence (section B) was also obtained on the effect on the bond (1:2) of the presence of the *cyclohexane* ring in the *spiro*-compounds. The expected effect is in the nature of an increase in strain, that is, a decrease in stability, and is small in magnitude. Actually we were not able to find a reagent which

would break this bond in a compound of the type VI (p. 322), and would not also break the same bond in one of the type V. This was, at any rate, in part, due to the fact that it did not appear to be possible to break the bond (1:2) in the series VI without first breaking the less stable bond (5:1). This, so far as it goes, is valuable, as it indicates that the effect of the *cyclohexane* ring on the bond (1:2) is of a smaller order than the effect on the bond (5:1). Fortunately, there is, however, a more precise and more delicate method of experiment. The *cyclohexanespiro*dicyclopentane structure VI was, in our experiments obtained from *cyclohexane*-1:1-diacetic acid by a method which involved first the closing of the *cyclopropane* ring, and then of the *cyclobutane* ring, by the establishment of the bond (3:4). Now the additional instability which we have been led to expect the bond (1:2) in the *spiro*-structure VI to exhibit is due to the tendency which there is, owing to the *cyclohexane* ring, for the angle between the bonds (1:4) and (1:5) to increase. It is obvious that this tendency will have greater effect if the bond (3:4) has not been established than would be the case if it had, for in the former case the tendency will not be resisted by the strained bonds of the *cyclobutane* ring. The result will be to magnify the effect by drawing further apart the carbon atoms (3) and (4) to an extent which might quite well be sufficiently great to make it appreciably more difficult to close the *cyclobutane* ring in the series VI than in the series V. A set of comparative experiments, made in order to discover whether such an effect could be detected, revealed its existence very clearly. The interest of these experiments lies in the fact that they show that the stresses in the *cyclohexane* ring have been communicated to the bond (1:2), a phenomenon which would seem necessarily to involve the assumption that the bond (5:1), as well as the carbon atoms (5) and (1), are in a state of strain.

With regard to the bond (1:4) in the structures V and VI (p. 322) there is available quite a good method of experiment, since sodium amalgam readily breaks this bond in certain substances belonging to these types without attacking in the slightest degree any of the other bonds in the molecules (see section E). The reductions occupy several hours, and can readily be conducted at constant temperature and under comparable conditions. By making comparative experiments along these lines it was discovered that, although the reactions proceeded in much the same way in the two cases, there was a considerable difference in the reaction velocities, the reductions proceeding more rapidly in the bridged-*spiro*-series VI than in the bridged-ring-series V. This is in agreement with the conclusions already reached on theoretical grounds (p. 327), but it



has also some interest from another point of view. It might be thought possible that valencies are so extremely elastic as to be capable of stretching as well as of bending. If that be so, the valency (1:4) ought to be less stretched out in the structure VI, in which the *cyclohexane* ring is tending to reduce the angle at which the bonds (5:1) and (5:4) emerge from the spirane carbon atom (5), than in the structure V, which contains no *cyclohexane* ring. Any such difference in the degree of elongation of the bond (1:4) ought to manifest itself as a marked difference of stability, since the forces between two carbon atoms must vary as some power, probably a high power, of the distance between them. As a matter of fact, the difference of stability which the reduction experiments reveal is in precisely the opposite sense from that which this view requires. This appears to us to show that no appreciable lengthening occurs, and that probably all carbon-to-carbon valencies have the same fixed length. It may also be noticed that the effect observed is the opposite to what would be expected if the bonds occupied inflexible straight lines. For in this case the tendency which the *cyclohexane* ring has to reduce the angle between the bonds (5:1) and (5:4) (compare Part I.) should operate in such a way as to increase the stability of the bond (1:4). These facts, therefore, constitute a strong argument in support of the conception of flexible valencies.

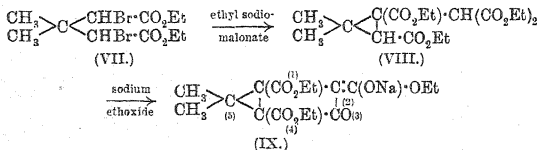
There remains to be mentioned finally a set of experiments which were undertaken in order to obtain information regarding the bond (2:3). This bond, according to the conclusions expressed on p. 327, should be practically unaffected by the strains in the *cyclohexane* ring. Actually we were not successful in finding a reagent which would attack this bond in a compound of the type VI, even when the stability of the bond was reduced by the introduction of an alkyl group at the carbon atom (2), without first attacking one of the *cyclopropane* bonds adjacent to the spirane carbon atom. However, the experiments were interesting as confirming our previous experiences regarding the instability of these bonds, and were in harmony with the conclusions already reached in regard to the insignificance of the effect which the *cyclohexane* should have on the bond (2:3).

In order to avoid confusion in what follows it ought perhaps to be pointed out that the bonds (5:1) and (5:4) are equivalent in the carbon skeletons V and VI (p. 322), and only become dissimilar when substituent groups are introduced unsymmetrically. This is actually the case with the compounds with which we have experimented, and it so happens that the bond split in all the substances which were subjected to fission by alkalis is, according to the method

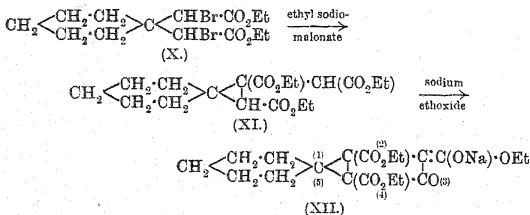
of numbering employed throughout, the bond (5:4), not the bond (5:1). This, it is clear, invalidates nothing, and, in fact, the agreement would be formal as well as actual if in the formulæ which follow we had numbered the *dicyclopentane* ring the other way round. The objection to doing this is that one would then meet with the same lack of formal consistency in regard to the bonds (1:2) and (3:4).

(B) *Formation of the Bridged-ring Systems V and VI* (p. 322):  
*Closing of the cycloButane Bond* (3:4).

Some time ago, in a paper published by one of us in conjunction with W. H. Perkin (T., 1901, **79**, 729), it was shown that when the dibromo-ester of  $\beta\beta$ -dimethylglutaric acid (VII) was treated with ethyl malonate and sodium ethoxide, condensation took place in two stages, the ultimate product being an insoluble, yellow sodium derivative of ethyl dimethyldicyclopentanonecarboxylate (IX). It was



therefore to be expected that if *cyclohexane*-1:1-diacetic acid were used in place of dimethylglutaric acid a similar condensation would ensue:



The sodium derivatives IX and XII clearly belong respectively to the types V and VI (p. 322), and it was therefore decided to make their formation and decompositions subjects of comparison.

It was found possible to prepare the sodium *spiro*-compound (XII) direct from ethyl dibromocyclohexanediacetate (X) and ethyl

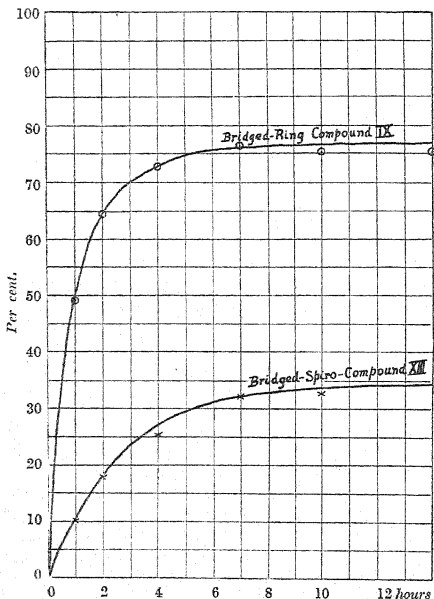
sodiummalonate under the same conditions as are employed in preparing the sodium ring compound (IX) from ethyl dibromodimethylglutarate (VII). Direct comparison of the two condensations is, however, complicated by the fact that, whilst ethyl dibromodimethylglutarate (VII) can readily be obtained in a state of purity by distillation, the corresponding *cyclohexane* derivative (X) decomposes when distilled. We were therefore forced to use a crude bromination product containing only 76–80 per cent. of the dibromo-ester. Nevertheless, the difference between the two cases is significant. Two experiments, one with the bromo-ester of dimethylglutaric acid, and the other with the bromo-ester of *cyclohexanediacetic* acid, carried out under comparable conditions (except that sufficient excess of the crude *cyclohexane* ester to allow for the impurities was used), gave in the first case a 62 per cent. yield of the sodium compound (IX, p. 330), and in the second a 13 per cent. yield of the sodium *spiro*-compound (XII, p. 330).

In order to make the comparison more definite, the tetraethyl ester XI (p. 330) was prepared in a state of purity. The internal condensations of the esters VIII and XI (p. 330) with alcoholic sodium ethoxide, whereby alcohol is eliminated and the bridged structure formed, were then carried out in a series of experiments made under comparable conditions. Several pairs of parallel experiments were made, in which the two esters were boiled with alcoholic sodium ethoxide under standard conditions for different lengths of time, at the end of which the insoluble sodium compounds were collected and weighed. The results are given in the experimental part of this paper (p. 359). The figures for the yields in the two cases lie upon fairly smooth but widely divergent curves (Fig. vii). These curves clearly show that the velocity of formation of the bridged-ring structure is much greater than the velocity of formation of the *spiro*-compound. The times required for a 20 per cent. conversion are in the ratio of approximately 10 to 1. An examination of the curves shows that, if  $x$  is the yield (per cent.) and  $t$  the time, the quantity  $-\partial/\partial x(dx/dt)$  is almost invariable with time and has a definite positive value for each curve, being about  $0.97^{-1}$  hours for the bridged-ring compound and about  $0.33^{-1}$  hour for the bridged-*spiro*-derivative. The velocity constants for the formation of the sodium compounds are therefore approximately in the ratio of 3 to 1. The best yields obtainable in the two cases are 77 per cent. and 38 per cent. respectively, but a longer time is necessary to produce a 38 per cent. yield of the *spiro*-compound than is required to obtain a 77 per cent. yield of the ring compound. The fact appears to be that the *spiro*-ester XI (p. 330) will only condense with itself when present in the sodium ethoxide

in considerable concentration. For, whereas under the experimental conditions which give the best yield (77 per cent.) of the sodio-ester, IX, the tetraethyl ester, VIII (p. 330), almost entirely disappears from the reaction mixture, when the ester XI is treated so as to produce a maximal yield of the sodio-*spiro*-ester (38 per cent.), then,

FIG. (vii).

*Establishment of the bond 3 : 4.*



although longer time is allowed in this case, the conversion is found to be only partial, about 15 per cent. of the tetraethyl ester being recoverable. Yet prolonging the time of reaction does not appear appreciably to increase the yield of sodium compound or reduce the quantity of tetraethyl ester recovered.

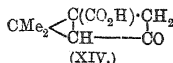
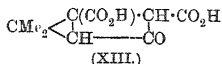
These experiments clearly show that it is more difficult to estab-

lish the bond (3:4) of the *cyclobutane* ring to form the *spiro*-compound XII than it is in the formation of the ring compound IX. Indeed, the low yield of the former compound was one of the greatest practical difficulties of the research.

(C) *Hydrolytic Decompositions of the Bridged-Ring Derivatives IX and XII* (p. 330): *Stability of the cycloPropane Bond* (4:5).

The first evidence of a difference of stability between compounds of the bridged-*spiro*-series VI and those of the bridged-ring series V (p. 322) was obtained in the course of some experiments on the hydrolysis of the sodium *spiro*-compound XII (p. 330).

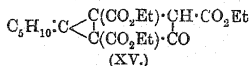
The effect of hydrolysing agents on the sodium compound IX has already been described in the paper with W. H. Perkin (*loc. cit.*), and the general conclusion reached was that the end-product of the action of alcoholic potassium hydroxide was a mixture of the dibasic and monobasic acids XIII and XIV, and that the same two acids



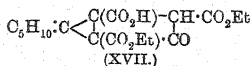
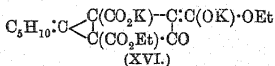
were formed by the action of dilute sulphuric acid. The dibasic acid XIII when heated with water in a sealed tube was found to yield the monobasic acid XIV.

On experimenting along these lines with the yellow sodium *spiro*-compound XII (p. 330) it soon became apparent that the *spiro*-compounds were behaving very differently; the hydrolytic products were therefore investigated in some detail.

When the yellow sodium *spiro*-compound XII was treated with cold dilute acid a colourless, solid ester,  $\text{C}_{19}\text{H}_{26}\text{O}_7$  (XV), was pro-



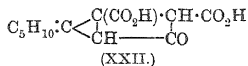
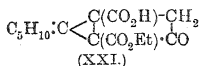
duced. This ester could be transformed by cold alcoholic potassium hydroxide into the yellow potassium salt, XVI, and thence by acids into the colourless acid-ester, XVII.



Regarding the question as to which of the three carbethoxyl groups has been attacked by the reagent, it is clear that it cannot be that attached to the carbon atom (2); for if it were, the forma-

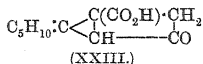


tiguous to the carbonyl group, and the products must therefore possess the constitutions XXI and XXII:



These formulæ are in complete accord with the properties of the substances. The acid-ester XXI, for example, melted without decomposition and gave no coloration with ferric chloride, showing that the free carboxyl group is not adjacent to the carbonyl group, and that the carboxyl group which was attached to the carbon atom (2) in the acid-ester XVIII has been removed. The dibasic acid XXII, on the other hand, melted with decomposition, gave a crimson colour with ferric chloride, and when treated with acetyl chloride gave an anhydride from which the original acid could be regenerated by treating with water. These facts clearly establish formula XXII.

The formation side by side of the acids XXI and XXII does not constitute quite the final stage of the hydrolysis by hydrochloric acid of the ethyl dihydrogen ester XVIII (p. 334). For the acid-ester XXI on prolonged boiling with hydrochloric acid loses its 4-carbethoxyl group, yielding the monocarboxylic acid, XXIII:

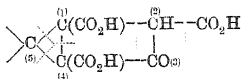


The dibasic acid XXII, on the other hand, was not changed appreciably even on boiling for eighty-seven hours with hydrochloric acid. The final product of the action of this reagent on the acid-ester XVIII was therefore a mixture of the dibasic acid and the monobasic acid (XXII and XXIII).

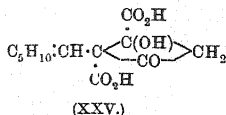
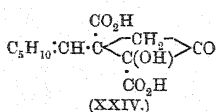
Further, the dibasic acid XXII was readily converted into the monobasic acid XXIII by heating for a few minutes at 200° with water. All the acid-esters (XVII, XVIII, and XXI) of the series reacted at this temperature with water, giving the same monobasic acid, usually in very good yield. The neutral triethyl ester XV (p. 333), however, required the presence of a trace of an acid, such as acetic or hydrochloric acid, in the water. The presence of a small quantity of butyric acid even was found to be quite sufficient, so that in the cases of the acid-esters the reaction is in all probability autocatalytic, the catalyst being the hydrogen ions produced initially by the electrolytic dissociation of the acid-esters themselves, and in the later stages of the reaction by the dissociation of the monocarboxylic acid XXIII or of carbonic acid. In the case of the

triethyl ester it is necessary artificially to introduce some hydrogen ions in order to start the reaction.

Alkaline hydrolysis of the acid-ester XVIII (p. 334) proceeded in quite a different direction, the product being an acid of the formula  $C_{12}H_{16}O_6$ . This substance is a dibasic acid. It is not an aldehyde, and contains no lactone ring. It is therefore a fission product formed by the breaking of one of the bonds (1:2), (1:4), (1:5), or (4:5) of the dicyclic system:



One of the three carboxyl groups originally present in the molecule has been lost, and, since the substance gives no colour reaction with ferric chloride, it is to be presumed that it is the carboxyl group attached to the carbon atom (2) which has disappeared. The question as to which of the four possible bonds has been broken is settled very clearly by the properties of the substance. Thus fission of the *cyclobutane* ring at the bond (1:2) should yield either a derivative containing an open-chain acetoacetic acid residue or a hydroxy-compound capable of forming a  $\gamma$ -lactone, according to the way in which the elements of water are added to the molecule at the point of fission. The substance actually obtained was found to be remarkably stable towards boiling alkalis and showed no tendency to pass into a lactone. On the other hand, although a *trans*-acid, it forms an anhydride with the greatest ease. For this reason it may be safely assumed that the 1- and the 4-carboxyl groups are attached to contiguous carbon atoms, and that the bridge-bond (1:4) has remained intact. The bond which has been broken is therefore one of the *cyclopropane* bonds (1:5) and (4:5), and since the substance is not a  $\gamma$ -hydroxy-acid, it must have one of the two following formulæ:



Although both these formulæ are in harmony with the properties of the substance, there can be little doubt that formula XXIV, and not formula XXV, is correct for this reason: The monobasic acid XXIII (p. 335) does not undergo fission with alcoholic potassium hydroxide. The fission therefore seems to be connected with the

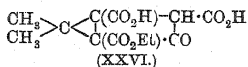


quaternary carbon atom in the position (4). If this be so it is reasonable to assume that splitting takes place at a point adjacent to this carbon atom. An indirect but interesting confirmation of this conclusion will subsequently be referred to (p. 345).

The substance to which the formula XXIV has been assigned separates from water with two molecules of water of crystallisation. The anhydrous compound when heated at  $250^{\circ}$  was found to pass into an anhydride which gave with water a new dibasic acid, also of the composition  $C_{12}H_{16}O_6$ . This did not take up water of crystallisation and melted with the immediate elimination of water-vapour. On boiling with hydrochloric acid, it was quantitatively converted into the isomeride previously mentioned. These relationships clearly indicate that geometrical isomerism of the *cis-trans*-type is here being encountered, both the acids  $C_{12}H_{16}O_6$  having the structure represented by the formula XXIV, which clearly requires the existence of this kind of isomerism.

The relationships between the various substances obtained by the hydrolysis of ethyl *cyclohexanespirodiacyclopentanetricarboxylate* and of its sodium derivative are collected together for convenience in table I.

In order to study more closely the contrast presented by the hydrolytic reactions in the dimethyldiacyclopentane and the *cyclohexanespirodiacyclopentane* series, a number of direct comparative experiments were made in order to determine the relative speeds at which the acid-esters of the two types decomposed in the presence of alkali. The substances chosen were the ethyl dihydrogen ester, XXVI,\* and the analogous substance in the bridged-



*spiro*-series, namely, the acid-ester XVIII (p. 334). The bridged-ring ester XXVI decomposes under the prolonged action of boiling alcoholic potassium hydroxide, yielding the monobasic acid XIV (p. 333). The bridged-*spiro*-ester XVIII, on the other hand, undergoes fission with the same reagent, giving the *cyclohexylcyclobutane* acid XXIV (p. 336).

There is, however, a remarkable difference in the ease with which the two reactions proceed. Thus in one pair of parallel experiments made under comparable conditions, the acid-ester XVIII of the bridged-*spiro*-series gave an 85 per cent. yield of the fission

\* This substance was not isolated during the earlier research. Its properties and mode of formation are therefore given in a note at the end of the experimental part of this paper.





product, whilst, on the contrary, the bridged-ring acid-ester XXVI was recovered unchanged to the extent of 93 per cent., only a trace of the monocarboxylic acid being isolated. No fission product of the dimethyldicyclopentane series was isolated in the course of these experiments.

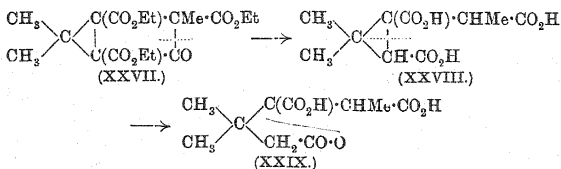
These experimental comparisons are interesting as showing the extraordinary facility with which the bond (4:5) in the bridged-*spiro*-series is broken. They have, however, interest from another point of view. For if they had not been made it would have been possible to advance an explanation of the difference in the ease of fission of the bond (4:5) in the two series, based, not on the strain effects of the *cyclohexane* ring, but on steric hindrance caused by the attached groups. It has already been noticed that it appears to be necessary to have a quaternary carbon atom in the position (4) in order to bring about the fission of the bond (4:5) by alkalis. One might assert, therefore, that in the bridged-*spiro*-series the  $C_5H_{10}$  group attached to the carbon atom (5) has the effect of preventing the elimination of the 4-carbethoxyl group. The carbon atoms (4) and (5), therefore, both remain quaternary in the presence of the alkaline reagent, and splitting occurs between them. One would have to assume, of course, that, although the steric effect of the  $C_5H_{10}$  group attached to the carbon atom (5) is sufficiently powerful to prevent the attack of the reagent on the 4-carbethoxyl group, yet, for some reason unknown, it does not inhibit the attack of the same reagent on the bond (4:5). In the bridged-ring series, on the contrary, the  $(CH_3)_2$  group attached to the carbon atom (5) might not have any appreciable steric effect. Splitting, therefore, might not take place in this case owing to the fact that when the acid-ester XXVI (p. 337) is treated with alcoholic potassium hydroxide, the 4-carbethoxyl group is so quickly eliminated that the carbon atom (4) becomes tertiary before the reagent has had time to react appreciably on the bond (4:5).

We were of the opinion at one time that there might be some truth in this way of explaining the phenomena, and it was the desire to test this hypothesis that furnished our chief motive for undertaking the comparative experiments with the acid-esters XXVI and XVIII. It will be seen, however, that the experiments effectively dispose of this explanation, since they show that the 4-carbethoxyl of the acid-ester XXVI is not at all readily eliminated under the experimental conditions employed. We consider this to be strong evidence that the bond (4:5) in the bridged-*spiro*-series is actually under considerable strain, much more so than in the bridged-ring series, and that the fission reactions are not to be accounted for as secondary phenomena due to

steric hindrance or other such causes. Several other examples of the splitting of the bond (4:5) in the bridged-*spiro*-series will subsequently be given (sections D and G).

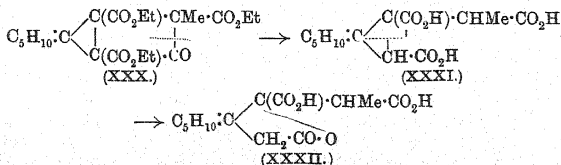
- (D) *Hydrolytic Decompositions of the Methylation Products of the Bridged-ring Derivatives IX and XII* (p. 330): *Stability of the cycloPropane Bond (4:5) and of the cycloButane Bond (2:3).*

In the paper on bridged-ring derivatives, to which reference has already been made, interesting results were obtained by methylating the yellow sodium compound IX (p. 330) and subjecting the methyl derivative to alkaline hydrolysis. It was found that the entrance of the methyl group at the carbon atom (2) in XXVII created a point of instability between the carbon atoms (2) and (3), and that fission took place with the formation, apparently, of the *cyclopropane* acid XXVIII, which then underwent a second fission, giving the dibasic lactonic acid XXIX.



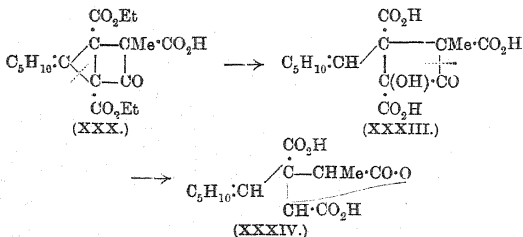
The sodium *spiro*-compound was quite readily methylated by means of methyl iodide. When the ester thus obtained was treated with alcoholic potassium hydroxide, the principal product was a dibasic lactonic acid, evidently a double-fission product, which, however, did not appear to be constituted analogously to the lactonic acid XXIX.

It would appear that there are two quite probable ways in which hydrolytic action might proceed. In the first place, the attack on the ester XXX might commence at the bond adjacent to the

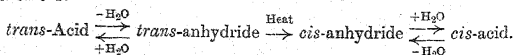


methylated residue and give as the first product a *spirocyclopropane* acid XXXI, which is similar to XXVIII, and would ultimately yield a lactonic acid XXXII strictly analogous to XXIX.

On the other hand, we know that the *cyclopropane* bond (4:5) is a very vulnerable point in the molecule of the unmethylated ester XV (p. 333), and it can scarcely be supposed that the entrance of a methyl group at the carbon atom (2) would stabilise it to any marked degree. If, in spite of the weakening of the bond (2:3) by the methyl group, the bond (4:5) still remains the most readily attacked part of the molecule, we should expect from the behaviour of the unmethylated ester to obtain a *cyclohexyl-cyclobutane* acid XXXIII, which would then split again, this time across the bond beside the methylated residue, giving ultimately a dibasic lactonic acid of the formula XXXIV.



In seeking evidence to enable us to decide between the formulæ XXXII and XXXIV, we made a study of the conditions of anhydride formation of the substance. It will be noticed that both formulæ represent substances which, as they have carboxyl groups attached to contiguous carbon atoms, ought easily to form anhydrides. A substance of the formula XXXII would, however, belong to the type of *aa'*-dimethylsuccinic acid, which yields two stereoisomeric anhydrides corresponding with the two stereoisomeric acids (Bone and Perkin, T., 1896, 69, 266). The *trans*-acid on treatment with acetyl chloride gives a *trans*-anhydride, which on distillation passes into the anhydride of the *cis*-acid, as shown in Scheme 1.

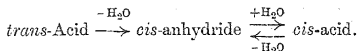


Scheme 1.

The lactonic acid XXIX (p. 341), to which XXXII is strictly analogous, actually does form two anhydrides related to one

another and to their acids in this way. Consequently, a substance of the formula XXXII should do the same.

On the other hand, in formula XXXIV, the bond uniting the two carboxyl-bearing carbon atoms forms part of a ring, and hence such a substance would be expected to dehydrate in the manner customary with carboxylated alicyclic compounds, the *trans*-acid, in which the carboxyl groups are on opposite sides of the ring, being incapable of forming its own anhydride, but passing on dehydration directly into the anhydride of the *cis*-acid, as indicated in Scheme 2.



Scheme 2.

Experiment showed that the lactonic acid obtained by the hydrolysis of the ester XXX (p. 342) actually dehydrated in accordance with Scheme 2. The original product of hydrolysis was the *trans*-acid. It did not eliminate water at the melting point, but was readily dehydrated by acetyl chloride. The anhydride formed was the same substance whether the product of dehydration was distilled or not, and on treatment with water yielded the *cis*-acid. This substance melted, with the immediate elimination of water vapour, and was instantly dehydrated by acetyl chloride. These facts point most distinctly to formula XXXIV (p. 342) as representing the true structure of the stereoisomeric acids.

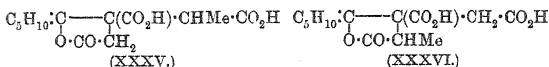
It is obvious, however, that we have by no means exhausted all the possible formulæ in the above considerations, since either of the intermediate compounds XXXI and XXXIII (pp. 341, 342) could split and take up water in a variety of ways. Indeed, besides XXXI and XXXIII, there are a number of other formulæ which the single-fission product might have. When, however, all these possibilities are examined, it would appear that there are only two formulæ besides XXXII and XXXIV (pp. 341, 342) which fulfil the following conditions relating to the *trans*-lactonic acid isolated:

(a) That it is a dibasic lactonic acid of the composition  $\text{C}_{13}\text{H}_{18}\text{O}_6$ , forming in neutral solution a silver salt,  $\text{C}_{13}\text{H}_{16}\text{O}_6\text{Ag}_2$ , and in alkaline solution a barium salt,  $(\text{C}_{13}\text{H}_{17}\text{O}_7)_2\text{Ba}_3$ .

(b) That its free carboxyl groups are attached to contiguous carbon atoms. We regard the behaviour of the substance on dehydration as a proof of this.

(c) That it is a  $\gamma$ -lactone. Experiment showed that there was an exceedingly strong tendency for the lactone ring to be formed, and in spite of many attempts we were unable to prepare the free hydroxy-acid.

The two formulæ which, along with XXXII and XXXIV, fulfil the above conditions are XXXV and XXXVI.



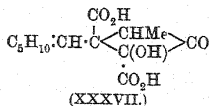
Of these, the first, XXXV, possesses an anhydride-forming group exactly similar to that of the lactonic acid XXXII (p. 341). A substance of the formula XXXV ought, therefore, for reasons given when XXXII was considered, to behave like *αα'*-dimethylsuccinic acid and like the acid XXIX (p. 341), and form anhydrides in accordance with Scheme 1.

The formula XXXVI, on the other hand, does not contain two asymmetric carbon atoms in its anhydride-forming group, and is therefore out of the question.

It will be seen that, of the four possible formulæ, XXXIV (p. 342) is the only one which accords with the facts of the case, namely, that the dehydration of the substance proceeds according to Scheme 2.

It may be added that the *cis*-lactonic acid is converted by boiling hydrochloric acid into the *trans*-isomeride, thus completing the cycle of transformations, which in Scheme 2 is only fragmentary.

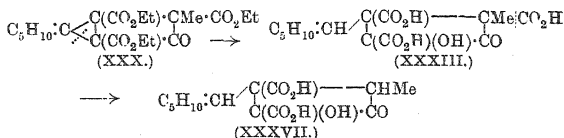
The *trans*-lactonic acid XXXIV (p. 342) was not the only product obtained by the alkaline hydrolysis of the methylated ester XXX (p. 342). There was always formed side by side with it a somewhat smaller quantity of a dibasic acid of the composition  $\text{C}_{13}\text{H}_{18}\text{O}_6$ . Both the dibasic acid and the lactonic acid appeared to be end-products of the reaction; that is to say, they were quite stable towards the reagent used in their preparation. The dibasic acid had properties practically identical with those of the dibasic acid  $\text{C}_{12}\text{H}_{16}\text{O}_6$  (XXIV, p. 336), which was obtained by the alkaline hydrolysis of the unmethylated ester XV (p. 333). It has therefore, without much doubt, been formed in a manner precisely analogous to that in which the acid XXIV was produced, and has the structure shown in the formula XXXVII.



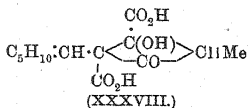
Like the parent substance XXIV, the homologous acid XXXVII was isolated in *cis*- and *trans*-forms, that originally obtained being the *trans*-form.



The formation side by side of the acids XXXIV (p. 342) and XXXVII (p. 344) is readily explained if we accept the view put forward on p. 342, that the *cyclopropane* bond (4:5) of the methylated ester XXX is the first point in the molecule attacked by the alkaline reagent. For, if this is so, the substance XXXIII which is first formed may undergo disruption beside the methylated residue in two ways, corresponding with the two hydrolytic decompositions of ethyl acetoacetate. It may either split the *cyclobutane* ring between the carbon atoms (2) and (3) to give the lactonic acid XXXIV, as shown on p. 342, or it may split between the methyl-bearing carbon atom and the attached carboxyl group, giving the acid XXXVII.



It is interesting once again to refer to the parent substance of which the acid XXXVII is the methyl derivative. It was noticed on p. 336 that formulæ XXIV and XXV were equally in harmony with the properties of the substance, but that for reasons there given formula XXIV was to be preferred. We have just seen that the formula which follows from this for the methylated substance enables us to explain the simultaneous production of this compound and of the lactonic acid XXXIV in a very straightforward manner. The alternative formula XXXVIII for the methylated



dibasic acid, strictly analogous to the formula XXV, has not this advantage. Such a substance could not be produced side by side with the lactonic acid XXXIV (p. 342), except as a result of the simultaneous occurrence of two totally different sets of reactions; also the lactonic acid which one might expect to be produced along with a compound of the formula XXXVIII would have properties different from those which the lactonic acid isolated was found to possess. We therefore think that we were right in selecting formula XXIV rather than XXV.

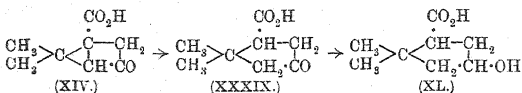
The results of the experiments on the alkaline hydrolysis of the

methylation product of the yellow sodium *spiro*-compound are summarised in table II.

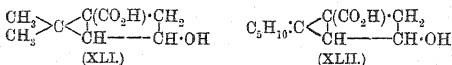
These experiments have an interest, inasmuch as they confirm, and even emphasise, the remarkable instability of the bond (4:5) in the bridged-*spiro*-series. For, in spite of the fact that the entrance of the methyl group at the carbon atom (2) of the methylated ester XXX creates a point of instability between the carbon atoms (2) and (3), the reagent commences its attack, not at the bond (2:3), but at the bond (4:5).

(E) *Reduction of the Monocarboxylated Bridged-ring Derivatives XIV and XXIII (pp. 333 and 335). Stability of the Bridge-bond (1:4).*

When the bridged-ring acid XIV is reduced by sodium amalgam, there is formed a *cyclopentane* acid XXXIX which contains two more atoms of hydrogen than the original acid. The reduction product is a ketonic acid, and on further reduction yields the corresponding hydroxy-acid XL. The fact that the ketonic acid has been formed by the addition of hydrogen at the bridge-bond (1:4) is shown (*loc. cit.*) by the production on oxidising with nitric acid of  $\beta\beta$ -dimethylglutaric acid and *as*-dimethylsuccinic acid. The reduction is therefore to be represented thus:



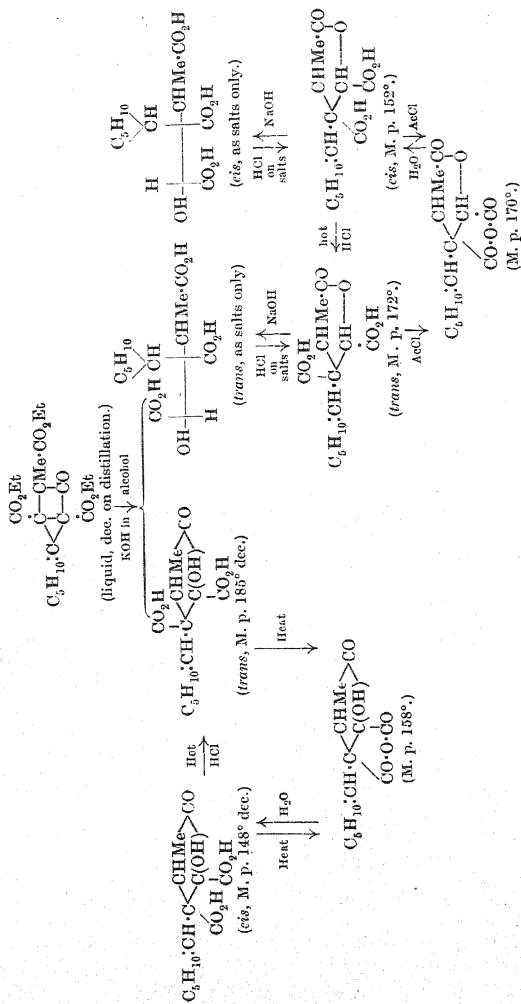
The remarkable feature of this reaction is that the bond (1:4) is actually more susceptible of attack by the reducing agent than is the carbonyl group, and that, consequently, the bridged hydroxy-acid XLI cannot be isolated.



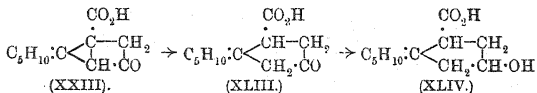
A series of experiments, using the monobasic acid XXIII, yielded precisely comparable results. In spite of careful search among the products of reductions carried out under varying conditions, no bridged hydroxy-acid of the formula XLII was isolated.

The first product of the action of sodium amalgam on the ketonic acid XXIII (p. 335) was a substance which contained two atoms of added hydrogen. It did not appear to react with acetyl chloride, but readily gave a semicarbazone. On subjecting it to further

TABLE II.



reduction by sodium amalgam, two more atoms of hydrogen were taken up, and there was formed a substance which gave an acetyl derivative on treatment with acetyl chloride. The successive reductions are therefore apparently analogous in the dimethyldicyclopentane and *cyclohexanespiro*dicyclopentane series, and in the latter case may be represented thus:



The fact that it was really the bond (1:4), and not the bond (4:5) or the bond (5:1), which had been broken by the reducing agent was clearly proved by the manner in which the reduced substances behaved with oxidising agents. These experiments are dealt with in Section F.

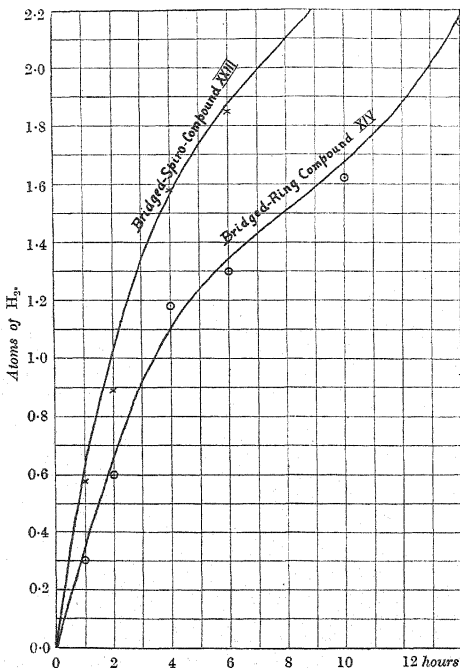
In our earliest experiments on the reduction of the bridged ketonic acid XXIII, we used conditions which were known to give a good yield of the reduced acid XXXIX when applied to the reduction of the bridged ketonic acid XIV. As a result, we obtained a product of indefinite melting point, which proved to be a mixture of the ketonic and hydroxy-acids XLIII and XLIV. It was therefore apparent that the reduction was proceeding more easily in the bridged-*spiro*-series than in the bridged-ring series.

In order to establish this point more definitely, a series of comparative experiments were instituted. In the first place, the bridged ketonic acid XIV (p. 333) was reduced under standard conditions for different lengths of time, and the products were isolated. They were, in general, a mixture of three acids, XIV, XXXIX, and XL. The proportion of hydroxyl group in this mixture was determined by estimating the acetic acid obtained by acetylation and subsequent hydrolysis. This method was found to give good results when applied to the pure hydroxy-acid XLIV. In this way, a certain time of reduction was discovered during which no appreciable quantity of hydroxy-acid was produced. The hydrogen content was determined by combustion, and it was found that the formation of hydroxy-acid began to be appreciable after the addition of about 1.7 atoms of hydrogen to the molecule. A similar set of experiments with the bridged ketonic acid of the *spiro*-series showed that the production of hydroxy-acid in this case became appreciable only after the addition of about 1.9 atoms of hydrogen to the molecule. The two bridged ketonic acids XIV and XXIII were then reduced under the same standard conditions for a certain length of time, the same in both cases, sufficiently short to ensure

that in neither case would any measurable amount of hydroxy-acid be formed. The products were then isolated and the hydrogen contents determined by combustion. Several pairs of experiments were made with different lengths of time, and the results obtained

FIG. (viii).

*Fission of the bridge-bond 1 : 4.*



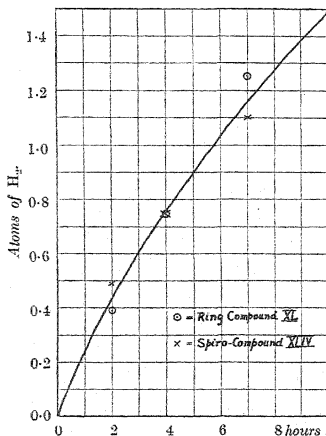
are given in the experimental part of this paper (p. 375). The figures lie fairly well on smooth but widely separated curves (Fig. viii), and, graphically interpolated, they show that if we take the time required for a 50 per cent. conversion, that is, the time during which the molecule of the bridged acid takes up one

atom of hydrogen, as the standard of comparison, then this time, in the case of the *spiro*-acid XXIII, is about 0.55 times as long as in the case of the ring derivative XIV. That is to say, the periods of half-change are in the ratio of approximately 1.8:1.

As a check on this result, the reduced acids XXXIX and XLIII (pp. 346 and 348) were prepared in a state of purity and further reduced under standard conditions for different lengths of time. The figures obtained in these experiments (p. 375) lie, with slight irregularities, on one and the same curve (Fig. ix). The periods

FIG. (ix).

*Reduction of the ketone group.*



of half-change are therefore as 1:1 as nearly as the experimental figures can be interpreted.

Thus there appears to be a very real difference in the ease of reduction of the monocarboxylic acids of the bridged-ring- and bridged-*spiro*-series. It will be noticed that the difference is in the sense anticipated from theoretical considerations (see Section A). It also would appear to be of the correct order of magnitude. For whilst the first-order effect, that on the bond (5:1), is manifested by a reaction which proceeds at a considerable speed in one series, but does not go at all in the other so far as

can be detected, both the second-order effects, that is, those on the bonds (1:2) and (1:4), exhibit themselves experimentally as moderate differences in reaction-velocities which are finite quantities in both the series. The third-order effect, that on the bond (2:3), was not detected experimentally.

(F) *Oxidation of the Fission-Products Derived from the Bridged-spiro-compound XII* (p. 330).

All the products of fission of the *cyclohexanespirocyclopentane* ring structure so far considered belong to one or other of the three following classes:

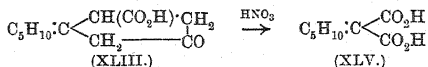
(1) Substances in which the bridge-bond (1:4) only has been broken.

(2) Those in which the *cyclopropane*-bond (4:5) only has been broken.

(3) Those in which the *cyclopropane*-bond (4:5) and the *cyclobutane*-bond (2:3) have both been broken.

In order, if possible, to obtain some confirmatory evidence regarding the constitutions of these substances, at least one typical example from each class was subjected to the action of oxidising agents.

In class (1) the first substance taken was the *cyclohexanespirocyclopentanone*-acid XLIII (p. 348). By far the most suitable reagent in this case is nitric acid. Dilute nitric acid, however, appears to have little action on the substance. With hot concentrated nitric acid a dibasic acid of the composition  $C_8H_{12}O_4$  was obtained. This substance when distilled gave off carbon dioxide with the formation of *cyclohexanecarboxylic* acid (hexahydrobenzoic acid). The dibasic acid is therefore evidently *cyclohexane-1:1-dicarboxylic* acid XLV. The same dicarboxylic acid was obtained

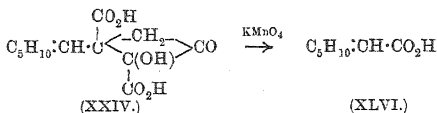


when the hydroxy-acid XLIV (p. 348) was used in place of the ketonic acid.

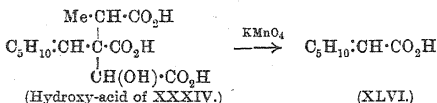
These experiments are interesting as leaving little room for doubt that the bond broken in the reduction of the bridged-ketonic acid XXIII (p. 335) was actually the bond (1:4).

The example taken from class (2) was the *trans-cyclohexylcyclobutane* acid XXIV (p. 336). In this case nitric acid appeared to be without effect. Warm alkaline permanganate was, however, quickly decolorised. The acid product was a liquid substance which

distilled apparently without a serious amount of decomposition and was identified as *cyclohexanecarboxylic acid* XLVI:



The member of the series (3) experimented on was the *trans-β-cyclohexyl-n-butane lactonic acid* XXXIV (p. 342). This acid was also unacted on by nitric acid, and required an alkaline solution of permanganate kept at above 70° to oxidise it at all rapidly. The product was, as in the former case, *cyclohexylcarboxylic acid*:



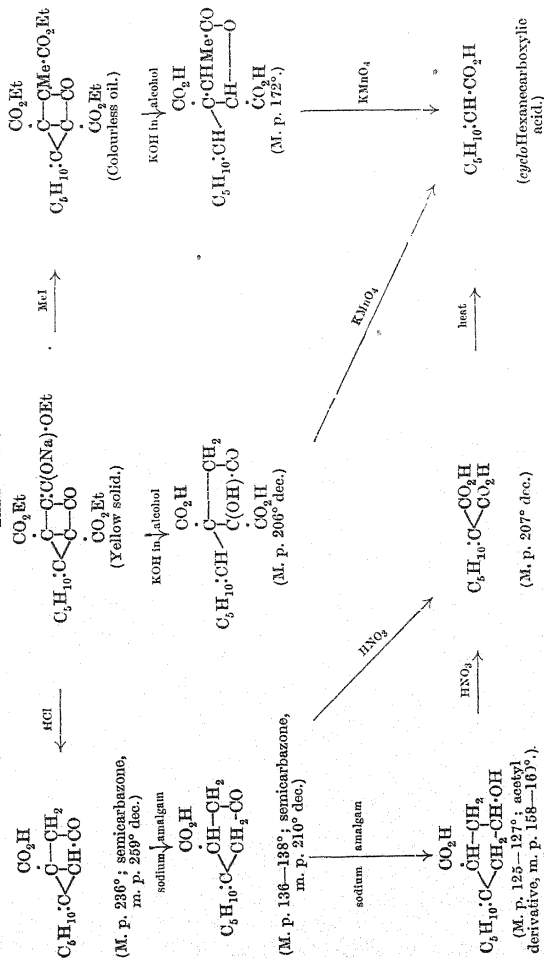
Both these oxidations with permanganate were carried out under various conditions, and in both cases the products were carefully examined for any traces of polybasic or lactonic acids, in which two side-chains might be attached to the *cyclohexane* carbon atom. No such products were detected, and, in view of the formulæ of the oxidised substances, none would be expected. On the other hand, if, for example, in the production of the *cyclohexylcyclobutane acid* XXIV (p. 336) some bond in the *dicyclopentane* structure other than one of those attached to the spirane carbon atom had been ruptured, one would expect to find products with two side-chains among the oxidation products.

The *cyclohexanecarboxylic acid* XLVI obtained in the course of the above experiments appeared on careful examination to be in all cases identical with the product obtained by the reduction of benzoic acid.

The various reactions by which the *dicyclopentane* ring in the original bridged-*spiro*-compound XII (p. 330) has been broken down forming ultimately *cyclohexanecarboxylic acid* are summarised for convenience in table III.

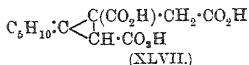


TABLE III.



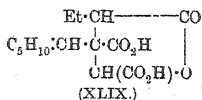
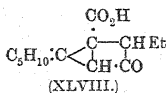
(G) *Examination of the By-products obtained in the Preparation of the Bridged-spiro-compound XII (p. 330): Isolation of Products of Fission Derived from this Substance through Side Reactions.*

During the preparation of the yellow sodium compound XII (p. 330) there was formed a considerable quantity of an oily by-product from which a number of acids were obtained by hydrolysis with hydrochloric acid. Amongst those isolated were *n*-butyric acid, cyclohexane-1:1-diacetic acid, and *trans*-cyclohexanespirocyclopropane-1:2-dicarboxylic acid. The formation of these acids is evidently traceable to the presence in the crude ethyl dibromocyclohexanediacetate used for the condensation of the corresponding monobromo-ester, of the unbrominated ester, and of ethyl bromide as impurities. There was also obtained a cyclohexanespirocyclopropane acid of the formula XLVII. This substance proved to be identical with the acid obtained by the action of acid hydrolysing

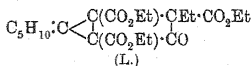


agents on the tetra-ethyl spirocyclopropane ester XI (p. 330), which clearly establishes the constitution of the compound.

In addition to the above-mentioned acids there were isolated two others to which the formulæ XLVIII and XLIX have been



assigned. These are clearly the products respectively of acid and of alkaline hydrolysis of the ethylated ester L. This ester is doubt-



less produced by the action of ethyl bromide on the yellow sodium compound XII, and apparently behaves towards alkaline hydrolysing agents similarly to the corresponding methylation product XXX (p. 342). We did not investigate the action of acids on the methyl derivative XXX, but the corresponding substance XXVII (p. 341) of the dimethyldicyclopentane series was found (*loc. cit.*) to yield with acid hydrolysing agents a monocarboxylic acid, to which XLVIII is strictly analogous.

The most interesting of these substances is the fission product XLIX of the ester L, and it is of interest to examine what possibilities there are of alkaline hydrolysis of the ester L taking place. No hydrolysis to a lactone of hydroxy-ester would be likely to occur in the anhydrous alcoholic solution in which the oily by-product was formed. The oil was, however, separated from the sodium compound XII by means of 95 per cent. alcohol, and, since some sodium ethoxide would certainly be adhering to the crude sodium compound, the alcoholic washings would contain sodium hydroxide, which must have brought about the fission of the ethylated ester L.

The lactonic acid XLIX was found to possess properties practically identical with those of its prototype, the fission product XXXIV (p. 342), of the methylated bridged ester XXX. Like the lactonic acid XXXIV, it was isolated in *cis*- and *trans*-forms, the substance originally obtained being the *trans*-form. One notable point of difference was noticed between these compounds and the methylated lactonic acids previously obtained. The ethylated *cis*-lactonic acid differed from the *trans*-form, and from both forms of the lactonic acid XXXIV, in the fact that it was found possible to isolate from it the free tribasic hydroxy-acid. This substance was, however, very unstable. It slowly gave up water when exposed to air at the ordinary temperature, the product being the *cis*-lactonic acid. On boiling with hydrochloric acid it was converted into the *trans*-lactonic acid. The other relationships between these ethylated products may be seen by reference to table IV, in which they are shown in relation to the ethylated ester L, the decompositions of which form another example of the great ease with which the bond (4:5) is ruptured by alkalis.

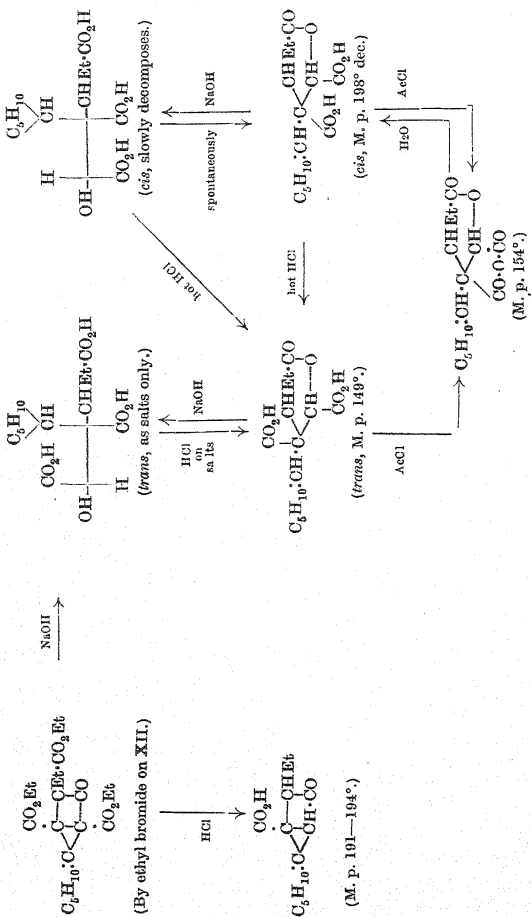
#### EXPERIMENTAL.

(a) *Condensation of Ethyl Dibromocyclohexane-1:1-diacetate with Ethyl Sodiomalonate.*

*cyclo*Hexane-1:1-diacetic acid was prepared for use in these experiments by the method given by Thole and Thorpe (T., 1911, 99, 422).

*Ethyl Dibromocyclohexane-1:1-diacetate.*—The bromination of the acid was effected by the Hell-Volhard-Zelinsky method as described in Part I. of this series. The neutral product contained about 80 per cent. of dibromo-ester.

TABLE IV.



*Ethyl cycloHexanespiro-1-methylcyclopropane-1:1':1':2-tetra-carboxylate* (XI, p. 330).

Forty-six grams of the crude dibromo-ester were added to a solution, in 60 grams of alcohol, of 4.6 grams of sodium and 32 grams of ethyl malonate. The solution was boiled for three hours, and then poured into dilute hydrochloric acid. The oil was extracted with ether and the extract washed with a solution of sodium carbonate, dried, and distilled.

The ester was obtained as a colourless liquid which on redistillation boiled at 250—260°/10 mm. On boiling with hydrochloric acid it was hydrolysed with the formation of the tricarboxylic acid (XLVII, p. 354), dealt with on p. 379:

0.1209 gave 0.2708 CO<sub>2</sub> and 0.0849 H<sub>2</sub>O. C=61.09; H=7.80.

C<sub>21</sub>H<sub>32</sub>O<sub>8</sub> requires C=61.2; H=7.8 per cent.

(b) *Formation of the Bridged-spiro-ester and its Sodium Compound.*

The formation of the bridged-spiro-compound by the condensation of the above-mentioned tetraethyl ester with itself has already been referred to in the Introduction (Section B). The compound was, however, usually prepared direct from the dibromo-ester by treating it with ethyl malonate and excess of sodium ethoxide. Many experiments were made in order to determine the best conditions.

*Ethyl Sodiocyclohexanespirodicyclopentan-3-one-1:2:4-tricarboxylate* (XII, p. 330).

Nine grams of sodium dissolved in 140 grams of absolute alcohol were treated with 30 grams of ethyl malonate. The solution was carefully under-cooled to about 35°, and 40 grams of dibromo-ester were gradually added, the temperature being kept below 40°. Half an hour after the addition was complete the liquid was heated on a steam-bath and kept boiling for thirty hours. At the end of that time the greater part of the alcohol was boiled off, and water added to the residue in the flask. The mixture was then shaken vigorously and filtered by the aid of the pump. In these circumstances the whole of the oil precipitated by the water adhered to the solid sodium compound. The filtrate, which gave no precipitate on acidification, was discarded. The purification of the sodium compound was effected by washing on the filter with 95 per cent. alcohol, and

finally by triturating with the same solvent until the weight of the dry solid was not altered on repeating the treatment. The alcoholic filtrates contained the oily by-product. (Section j, p. 377.)

The sodium compound was obtained as a bright yellow insoluble substance which gave a crimson colour with aqueous ferric chloride containing a trace of alcohol:

0.3132 gave 0.0590  $\text{Na}_2\text{SO}_4$ .  $\text{Na} = 6.10$ .

$\text{C}_{19}\text{H}_{25}\text{O}_7\text{Na}$  requires  $\text{Na} = 5.93$  per cent.

*Ethyl cycloHexanespirodicyclopentan-3-one-1:2:4-tricarboxylate* (XV, p. 333).

When the yellow sodium compound was shaken with cold dilute aqueous hydrochloric acid and ether it passed quickly into solution, the yellow colour being discharged. The ethereal layer, on drying and evaporating the solvent, yielded a mass of crystals melting at  $46-47^\circ$ .

The ester was exceedingly readily soluble in the usual organic solvents, and did not appear capable of being easily recrystallised. It gave a crimson colour with ferric chloride, and on treating with cold aqueous sodium hydroxide yielded the original sodium compound:

0.1331 gave 0.3036  $\text{CO}_2$  and 0.0842  $\text{H}_2\text{O}$ .  $\text{C} = 62.21$ ;  $\text{H} = 7.03$ .

$\text{C}_{19}\text{H}_{26}\text{O}_7$  requires  $\text{C} = 62.3$ ;  $\text{H} = 7.1$  per cent.

(c) *Comparative Experiments on the Formation of the Bridged-ring- and Bridged-spiro-compounds* (IX and XII, p. 330).

$\beta\beta$ -Dimethylglutaric acid was prepared by the method of Thole and Thorpe (T., 1911, **99**, 422).

*Ethyl Dibromodimethylglutarate*.—The acid was first converted into its anhydride (T., 1899, **75**, 48), which was then brominated (T., 1901, **79**, 776). The dibromo-ester was redistilled and collected for use in subsequent experiments at  $182-185^\circ/24$  mm.

*Ethyl 1:3:3-Trimethylcyclopropane-1:1':1':2-tetracarboxylate*.

This ester was prepared by condensing the dibromo-ester with ethyl sodiomalonate in alcoholic solution under the conditions used by Perkin and Thorpe (*ibid.*) and purified by distillation, the fraction boiling at  $231-236^\circ/34$  mm. being taken as sufficiently pure for the experiments hereunder described.

Ethyl trimethylcyclopropanetetracarboxylate and ethyl cyclo-

hexanespiromethylcyclopropanetetracarboxylate were then employed in a series of experiments, which were carried out with the object of determining the relative speeds with which the two esters underwent internal condensation in the presence of sodium ethoxide. The method was as follows: One molecular proportion of each ester was treated with two atomic proportions of sodium dissolved in fifteen molecular proportions of absolute ethyl alcohol. The solutions were kept in a thermostat for known lengths of time, after which the alcohol was boiled off under diminished pressure, and water was added. The precipitates were then collected, washed with alcohol, dried, and weighed.

The following percentage yields of the sodium compounds IX and XII (p. 330) were obtained, the temperature being 75°:

TABLE V.

Time (hours).	Bridged-ring- compound, IX. (Per cent.)	Bridged-spiro- compound, XII. (Per cent.)
1.0	49.8	10.1
2.0	64.7	17.9
4.0	73.0	25.5
7.0	76.6	32.4
10.0	75.3	32.9
14.0	75.3	—
24.0	—	37.7

(d) *Hydrolysis of the Bridged-spiro-ester and of its Yellow Sodium Compound.*

The remarkable diversity in the characters of the substances which can be obtained by hydrolysing the yellow sodium spiro-compound or the corresponding free ester under different conditions has already been alluded to in the Introduction. The following is a summary of the principal experimental details.

*Diethyl Potassium Potassiocyclohexanespiroindicyclopentan-3-one-1:2:4-tricarboxylate (XVI, p. 333).*

When the original yellow sodium compound was left in contact with cold alcoholic potassium hydroxide for ten hours, it gradually dissolved, and a canary-yellow potassium salt separated.

This compound was found to be insoluble in water, but quite appreciably soluble in methyl alcohol. When recrystallised from a large bulk of this solvent, it separated in long, yellow needles, which gave a violet colour with ferric chloride:

0.1354 gave 0.0580  $\text{K}_2\text{SO}_4$ .  $\text{K} = 19.16$ .

$\text{C}_{17}\text{H}_{20}\text{O}_7\text{K}_2$  requires  $\text{K} = 18.8$  per cent.

*Diethyl Hydrogen cycloHexanespirodi-cyclopentan-3-one-  
1:2:4-tricarboxylate* (XVII, p. 333).

When the potassium salt was treated with cold dilute hydrochloric acid, a gummy precipitate was obtained. This could not be induced to crystallise, and on distillation underwent extensive decomposition. It was therefore extracted with pure ether, and, after drying and evaporating the solvent, left for some days in an exhausted desiccator:

0.1249 gave 0.2751  $\text{CO}_2$  and 0.0730  $\text{H}_2\text{O}$ .  $\text{C}=60.07$ ;  $\text{H}=6.50$ .

$\text{C}_{17}\text{H}_{22}\text{O}_7$  requires  $\text{C}=60.4$ ;  $\text{H}=6.5$  per cent.

This acid-ester is also the first product of the action of boiling hydrochloric acid on the triethyl ester (XV, p. 333), as is proved by the following experiment. The yellow sodium compound was boiled with 20 per cent. hydrochloric acid for one hour. The liquid was evaporated, and the residue dissolved in the minimal quantity of water. The hot aqueous solution was rapidly cooled, and the oily precipitate which separated was collected by pouring the liquid through a wet filter. The oil on the filter was then washed through with alcohol, and caused to crystallise as completely as possible from 15 per cent. alcohol. The crystals consisted of the ethyl hydrogen ester XXI (p. 335). The ultimate oily residue from these crystallisations was dissolved in methyl alcohol and treated with a slight excess of cold methyl-alcoholic potassium hydroxide. The yellow precipitate which immediately separated was collected and recrystallised from methyl alcohol. On analysis, it gave  $\text{K}=19.03$ , whilst the free acid-ester obtained on acidification gave  $\text{C}=60.21$ ,  $\text{H}=6.60$  per cent.

With ferric chloride, the acid-ester gave a violet coloration. Cold methyl-alcoholic potassium hydroxide converted it into the potassium compound. It distilled at about  $200\text{--}260^\circ/23\text{ mm.}$ , with, however, considerable decomposition. Attempts were made to hydrolyse the gummy distillate both by acids and by alkalis, but no pure substance was isolated from the products.

*Ethyl Dihydrogen cycloHexanespirodi-cyclopentan-3-one-  
1:2:4-tricarboxylate* (XVIII, p. 334).

Five grams of the yellow sodium compound were suspended in 20 c.c. of 3*N*-ethyl-alcoholic potassium hydroxide, and the mixture was boiled until the yellow colour was discharged. The colourless precipitate, which was very hygroscopic, was collected as rapidly as possible and drained on porous porcelain in a desiccator. It



was then dissolved in a small quantity of water and decomposed with hydrochloric acid. The acid which separated out was re-crystallised from water. The potassium salt XVI may be used in place of the sodium compound in this preparation.

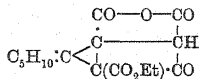
The same acid-ester may also be obtained by acid hydrolysis of the triethyl ester (XV, p. 333) or of its sodium compound. Thus, when the sodium compound was boiled for one hour with 20 per cent. hydrochloric acid, and the acid-esters XVII and XXI separated by precipitating them together as an oil in the manner described on p. 360, it was found that in the filtrate from the oil there were present two crystalline substances. These were isolated by treating the solution, after concentration, with sufficient concentrated hydrochloric acid to clear the turbidity. The crystals which were then deposited from solution were separated by fractionally crystallising from water into the acid-ester XVIII and the dibasic acid XXII, the latter being the more readily soluble.

The acid-ester formed long, colourless needles, which melted and decomposed at 206°. It gave a bluish-violet colour with ferric chloride:

0.1298 gave 0.2745 CO<sub>2</sub> and 0.0683 H<sub>2</sub>O. C=57.68; H=5.84.

C<sub>15</sub>H<sub>18</sub>O<sub>7</sub> requires C=58.1; H=5.8 per cent.

The *anhydro-ester*,



was prepared by treating the acid-ester at 100° for one hour with acetyl chloride in a closed flask. The residue obtained on evaporation was crystallised from ether. The crystalline anhydride melted at 126°, and was converted into the original acid-ester on boiling with water:

0.0751 gave 0.1705 CO<sub>2</sub> and 0.0385 H<sub>2</sub>O. C=61.92; H=5.70.

C<sub>15</sub>H<sub>16</sub>O<sub>6</sub> requires C=61.6; H=5.5 per cent.

*Ethyl Hydrogen 5-cycloHexanespirodicyclopentan-3-one-1:4-dicarboxylate* (XXI, p. 335).

The formation of this substance has already been alluded to on p. 360. It is best prepared by boiling the triethyl ester (XV, p. 333) with 20 per cent. hydrochloric acid for five hours, or by boiling the acid-ester (XVIII, p. 334) with the same reagent for two hours. In either case, the product obtained on evaporation was found to be a mixture of three acids. It was crystallised from

the minimal quantity of boiling 50 per cent. ethyl alcohol. The crystals which separated consisted principally of the monobasic acid (XXIII, p. 335), and were collected, the filtrate being then evaporated until most of the alcohol had been removed. It was then cooled as rapidly as possible, and the oil which separated was collected on a wet filter. The filtrate, on concentrating and mixing with concentrated hydrochloric acid, deposited the dibasic acid (XXII, p. 335). The oil on the filter was dissolved in alcohol and recrystallised several times from a mixture of alcohol and water.

The acid-ester obtained in this way melted at 104–106°, and gave no colour with ferric chloride. It did not decompose appreciably when heated to 250°:

0.0887 gave 0.2061  $\text{CO}_2$  and 0.0548  $\text{H}_2\text{O}$ .  $\text{C}=63.37$ ;  $\text{H}=6.88$ .

$\text{C}_{14}\text{H}_{18}\text{O}_5$  requires  $\text{C}=63.2$ ;  $\text{H}=6.8$  per cent.

0.1200 required 18.62 c.c. of  $\text{Ba}(\text{OH})_2$  solution (0.0243*N*) for neutralisation.  $\text{C}_{14}\text{H}_{18}\text{O}_5$  (monobasic) requires 18.6 c.c.

*5-cycloHexanespirodi-cyclopentan-3-one-1:2-dicarboxylic Acid*  
(XXII, p. 335).

The formation of this substance as a by-product in the preparation of the various acid-esters of the series has already been noticed. It was found to be produced in good yield by boiling either the yellow sodium compound or the acid-ester (XVIII, p. 334) with 10 parts by weight of 20 per cent. aqueous hydrochloric acid for twelve hours. As the boiling proceeded, oily products separated out, and subsequently passed again into solution. Then crystals appeared in the boiling liquid. At the end of the period, the mixture was cooled and allowed to remain at the ordinary temperature for twenty-four hours, after which practically the whole of the organic material had crystallised out. The crystalline mixture consisted of about three parts of the dibasic acid XXII to one part of the monobasic acid XXIII (p. 335). It was boiled with four times its weight of water, and the suspension cautiously cooled and quickly filtered. By this means, the monobasic acid was separated almost quantitatively from a solution which, in the cold, was supersaturated with respect to the dibasic acid. The agitation caused by filtering usually caused the filtrate to set to a stiff paste of crystals of the dibasic acid. These were recrystallised from water.

The acid separated from water in rosettes of long, silky, needle-shaped crystals, which melted and decomposed at 234°. It gave a deep crimson colour with ferric chloride, but did not appear to be acted on when boiled with hydrochloric acid for several days:

0.1087 gave 0.2407  $\text{CO}_2$  and 0.0584  $\text{H}_2\text{O}$ .  $\text{C}=60.39$ ;  $\text{H}=5.97$ .

$\text{C}_{12}\text{H}_{14}\text{O}_5$  requires  $\text{C}=60.5$ ;  $\text{H}=5.9$  per cent.

0.0715 required 24.65 c.c.  $\text{Ba}(\text{OH})_2$  solution (0.0243*N*) for neutralisation.  $\text{C}_{12}\text{H}_{14}\text{O}_5$  (dibasic) requires 24.7 c.c.

CO-O-CO  
 $\text{C} \begin{array}{l} \nearrow \text{CH} \\ \searrow \text{CH} \end{array}$

The anhydride,  $\text{C}_5\text{H}_{12}\text{O}_4$ , was produced when the

free acid was treated with acetyl chloride at  $100^\circ$  in a closed flask. The solid residue obtained on evaporation was triturated with aqueous sodium hydrogen carbonate and recrystallised from ether. It melted at  $154^\circ$ , and on treating with aqueous sodium hydroxide gave the sodium salt of the original dibasic acid:

0.1050 gave 0.2515  $\text{CO}_2$  and 0.0518  $\text{H}_2\text{O}$ .  $\text{C}=65.32$ ;  $\text{H}=5.48$ .

$\text{C}_{12}\text{H}_{12}\text{O}_4$  requires  $\text{C}=65.5$ ;  $\text{H}=5.5$  per cent.

*5-cycloHexanespiroindicyclopentan-3-one-1-carboxylic Acid*  
 (XXIII, p. 335).

A mixture of about one part of this acid to three parts of the dibasic acid (XXII, p. 335) was formed when either the triethyl ester, XV, or its sodium compound, or the diethyl hydrogen ester, XVII, or its potassium compound, or the ethyl dihydrogen ester, XVIII, was boiled for twelve hours with 20 per cent. hydrochloric acid. The ethyl hydrogen ester XXI was found to be converted quantitatively into the monobasic acid by boiling hydrochloric acid. The dibasic acid XXII, on the other hand, did not appear to be affected by this reagent.

The dibasic acid, when heated above its melting point, however, evolved carbon dioxide, and from the dark-coloured residue a small amount of monobasic acid could be isolated. A good yield was obtained when the dibasic acid was heated with water at  $200^\circ$  for about ten minutes. The acid-esters XVII and XVIII also gave excellent yields of the monobasic acid when treated in this way. The triethyl ester XV, however, required the presence of a trace of acid in the water. A small quantity of hydrochloric acid or acetic acid, or even of butyric acid, was found to be sufficient.

The most convenient way of preparing the monobasic acid is by heating the yellow sodium compound with a slight excess of dilute hydrochloric acid at  $200^\circ$ . When preparing considerable quantities, however, it was found desirable to drive off as much carbon dioxide and alcohol as possible before closing the vessel. The

sodium compound, in portions of about 10 grams, was boiled with ten times its weight of 20 per cent. hydrochloric acid for twelve hours in a strong flask provided with a short reflux air-condenser. Enough aqueous sodium hydroxide was then added to reduce the concentration of free mineral acid to 2 or 3 per cent., and the solution was again boiled to expel the air. The flask was then securely corked and immersed in an oil-bath at  $200^{\circ}$  for ten minutes. After cooling to the ordinary temperature, the crystals were collected and recrystallised from 96 per cent. alcohol, using a little animal charcoal to remove the dark impurities. The yield was 85 per cent.

The monobasic acid was sparingly soluble in hot or cold water and in most cold organic solvents, but it crystallised well from hot ethyl alcohol in long needles. It melted at  $236^{\circ}$  without decomposition, and gave no colour with ferric chloride. It was found to be unacted on by boiling aqueous or alcoholic potassium hydroxide, and by prolonged boiling with hydrochloric acid. Cold alkaline permanganate was, however, instantly decolorised:

0.1337 gave 0.3310  $\text{CO}_2$  and 0.0860  $\text{H}_2\text{O}$ .  $\text{C}=67.52$ ;  $\text{H}=7.14$ .

$\text{C}_{11}\text{H}_{14}\text{O}_8$  requires  $\text{C}=68.0$ ;  $\text{H}=7.2$  per cent.

The semicarbazone,  $\text{C}_5\text{H}_{10}:\text{C} \begin{array}{l} \text{C}(\text{CO}_2\text{H})\cdot\text{CH}_2 \\ \text{CH} \longrightarrow \text{C}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 \end{array}$ , was prepared by boiling the acid with an aqueous solution of semicarbazide acetate for a few seconds. On cooling the solution, the semicarbazone separated out, and was recrystallised from alcohol. It melted and decomposed at  $259^{\circ}$ :

0.1071 gave 0.2240  $\text{CO}_2$  and 0.0661  $\text{H}_2\text{O}$ .  $\text{C}=57.04$ ;  $\text{H}=6.85$ .

$\text{C}_{12}\text{H}_{17}\text{O}_8\text{N}_3$  requires  $\text{C}=57.4$ ;  $\text{H}=6.8$  per cent.

*trans-3-Hydroxy-4-cyclohexylcyclobutan-2-one-3:4-dicarboxylic Acid (XXIV, p. 336).*

Five grams of the yellow sodium compound were boiled with 30 c.c. of 4*N*-alcoholic potassium hydroxide, the boiling being continued for one hour after the suspended matter had become colourless; or, alternatively, 5 grams of the acid-ester (XVIII, p. 334) were boiled with 30 c.c. of the same reagent for one hour. In either case, the product was isolated by evaporating the alcohol and adding water and hydrochloric acid. The acid solution was extracted ten times with its own volume of ether, and the extract dried over calcium chloride for at least three days. This was found to be necessary, since the acid was present in the ether in its hydrated form, which apparently gave up water to the calcium chloride very slowly, and incomplete dehydration interfered with

the subsequent purification. When quite dry, the ether was evaporated and the viscid residue triturated with chloroform. The crystals which were caused to separate by this treatment were drained on porous porcelain and washed with fresh ether.

The acid prepared in this way was fairly pure and melted and decomposed at  $203^{\circ}$ . It was very readily soluble in water and in all the usual organic solvents, except chloroform and light petroleum. In these solvents it was only sparingly soluble, but it did not appear to crystallise well from mixtures of solvents. It gave no colour with ferric chloride, and did not appear to be acted on by boiling acetyl chloride (compare Part I). The acid was purified for analysis through the hydrate (see below):

0.1331 gave  $0.2734 \text{ CO}_2$  and  $0.0748 \text{ H}_2\text{O}$ .  $\text{C}=56.02$ ;  $\text{H}=6.24$ .

$\text{C}_{12}\text{H}_{16}\text{O}_6$  requires  $\text{C}=56.2$ ;  $\text{H}=6.2$  per cent.

0.0352 required  $11.25$  c.c.  $\text{Ba}(\text{OH})_2$  solution ( $0.0243N$ ) for neutralisation.  $\text{C}_{12}\text{H}_{16}\text{O}_6$  (dibasic) requires  $11.3$  c.c.

The *hydrated* form,  $\text{C}_{12}\text{H}_{16}\text{O}_6 \cdot 2\text{H}_2\text{O}$ , separated in large, dense prisms when the anhydrous acid was dissolved in hot water and the solution cooled. The hydrated acid readily dissolved in dry ether, and was much more readily soluble in chloroform than the anhydrous substance. At  $100^{\circ}$ , it evolved water vapour, leaving the anhydrous acid in a very pure form, melting at  $206^{\circ}$  to a colourless liquid, which evolved steam, and, after cooling, set to a solid mass, which melted at about  $135^{\circ}$ :

0.1648 lost  $0.0201$  at  $100^{\circ}$ .  $\text{H}_2\text{O}=12.20$ .

$\text{C}_{12}\text{H}_{16}\text{O}_6 \cdot 2\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}=12.3$  per cent.

The *silver* salt was precipitated by silver nitrate from a neutral solution of the ammonium salt:

0.1435 gave  $0.0656 \text{ Ag}$ .  $\text{Ag}=45.71$ .

0.1729 ,,  $0.1929 \text{ CO}_2$  and  $0.0473 \text{ H}_2\text{O}$ .  $\text{C}=30.43$ ;  $\text{H}=3.03$ .

$\text{C}_{12}\text{H}_{14}\text{O}_6\text{Ag}_2$  requires  $\text{C}=30.6$ ;  $\text{H}=3.0$ ;  $\text{Ag}=45.9$  per cent.

The *barium* salt was precipitated from a solution of the acid in water by adding an excess of barium hydroxide:

0.1007 gave  $0.0595 \text{ BaSO}_4$ .  $\text{Ba}=34.74$ .

$\text{C}_{12}\text{H}_{14}\text{O}_6\text{Ba}$  requires  $\text{Ba}=35.1$  per cent.

*cis*-3-Hydroxy-4-cyclohexylcyclobutan-2-one-3:4-dicarboxylic  
Acid (XXIV, p. 336).

This acid was prepared by dissolving its anhydride (see below) in a slight excess of  $4N$ -aqueous sodium hydroxide and then adding a slight excess of concentrated hydrochloric acid. The precipitated acid was collected and dried. It was then dissolved in

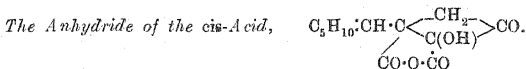
dry ether containing a trace of alcohol, and caused to crystallise from this solution by adding benzene. The crystals were finally purified by triturating with pure dry ether and again recrystallising from a mixture of ether and benzene containing alcohol.

The pure *cis*-acid melted at  $145^{\circ}$ , and rapidly evolved water vapour. It readily dissolved in water or alcohol, but was almost insoluble in pure dry ether. Unlike the *trans*-form, it did not appear to take up water of crystallisation:

0.0929 gave 0.1912  $\text{CO}_2$  and 0.0548  $\text{H}_2\text{O}$ .  $\text{C}=56.13$ ;  $\text{H}=6.55$ .

$\text{C}_{12}\text{H}_{16}\text{O}_6$  requires  $\text{C}=56.3$ ;  $\text{H}=6.3$  per cent.

0.0446 required 14.40 c.c.  $\text{Ba}(\text{OH})_2$  solution (0.0243*N*) for neutralisation.  $\text{C}_{12}\text{H}_{16}\text{O}_6$  (dibasic) requires 14.3 c.c.

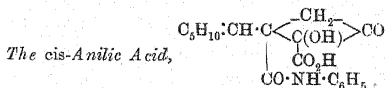


The *trans*-acid, on heating above its melting point, gave off water vapour. The transformation was, however, by no means complete unless the fused material was raised to  $240\text{--}250^{\circ}$  and maintained at this temperature until it began to darken in colour. The product solidified on cooling, and, after triturating with aqueous sodium hydrogen carbonate and drying, was recrystallised from dry ether. It separated in large, oblique prisms which melted at  $155^{\circ}$ . The substance was also recrystallised from benzene.

The same anhydride was obtained by heating the *cis*-acid above its melting point:

0.1335 gave 0.2959  $\text{CO}_2$  and 0.0709  $\text{H}_2\text{O}$ .  $\text{C}=60.45$ ;  $\text{H}=5.90$ .

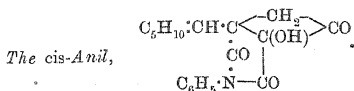
$\text{C}_{12}\text{H}_{14}\text{O}_5$  requires  $\text{C}=60.5$ ;  $\text{H}=5.9$  per cent.



This substance was at once precipitated when the *cis*-anhydride was dissolved in benzene and treated with a solution of aniline in the same solvent. It was purified by first triturating with ether and then recrystallising from dilute alcohol. It separated in minute crystals, which melted and decomposed at  $202^{\circ}$ :

0.1145 gave 0.2721  $\text{CO}_2$  and 0.0666  $\text{H}_2\text{O}$ .  $\text{C}=64.81$ ;  $\text{H}=6.46$ .

$\text{C}_{18}\text{H}_{21}\text{O}_6\text{N}$  requires  $\text{C}=65.3$ ;  $\text{H}=6.3$  per cent.



The *cis*-anil was readily obtained by heating the anilic acid at  $210^\circ$  until the evolution of steam had ceased. The product was triturated with sodium hydrogen carbonate and then recrystallised from absolute alcohol. It separated in long, silky needles which melted at  $199^\circ$ :

0.1098 gave 0.2778  $\text{CO}_2$  and 0.0592  $\text{H}_2\text{O}$ .  $\text{C} = 69.00$ ;  $\text{H} = 5.99$ .

$\text{C}_{18}\text{H}_{19}\text{O}_4\text{N}$  requires  $\text{C} = 69.0$ ;  $\text{H} = 6.1$  per cent.

(e) *Comparative Experiments with the Acid-Esters* (XXVI, p. 337, and XVIII, p. 334) of the Dimethyldicyclopentane and cycloHexanespirodicyclopentane Series.\*

One molecular proportion of each acid-ester was boiled for fifteen minutes with 6 molecular proportions of potassium hydroxide in 3.6*N*-solution in ethyl alcohol. The bulk of the alcohol was evaporated under diminished pressure and water and excess of hydrochloric acid were added to the residue. The acid products were then extracted quantitatively with ether. The percentage yields were as follows:

TABLE VI.

Bridged-ring-acid-ester XXVI.			Bridged-spiro-acid-ester XVIII.		
Acid-ester recovered.	Monocarboxylic acid formed.	Fission product formed.	Acid-ester recovered.	Products of loss of 4-carbethoxyl group.	Fission products formed.
85	1.5	0	0	0	85
81	4	0	5	0	78

In all cases a small quantity of gummy material was formed, and for this reason the whole of the original material was never accounted for as crystalline products. The small quantity of monocarboxylic acid XIV was readily isolated by reason of its sparing solubility in cold water. The recovered acid-ester XVIII was also quite easily separated from the fission product by means of dry chloroform in which the latter, if quite anhydrous, is almost insoluble.

\* See note, p. 337.

(f) *Preparation and Hydrolysis of the Methylation Product of the Yellow Sodium spiro-Compound* (XII, p. 330).

The yellow sodium compound does not react at all readily with methyl iodide under the usual conditions even at  $100^{\circ}$  in a closed flask. If, however, four or five times the theoretical quantity of methyl iodide is used, methylation proceeds rapidly.

*Ethyl cycloHexanespiro-2-methyldicyclopentan-3-one-1:2:4-tricarboxylate* (XXX, p. 342).

Twenty grams of the yellow sodium compound were heated with a solution of 20 grams of methyl iodide in 100 grams of absolute alcohol at  $100^{\circ}$  for one and a-half hours in a closed flask, which, from time to time, was vigorously shaken. The excess of the methyl iodide and most of the alcohol were then distilled off and the residue poured into 400 c.c. of water. The precipitated oil was extracted with ether, the extract being washed with water and sodium carbonate solution, dried, and evaporated. The oily residue was found to decompose on attempting to distil it under diminished pressure. It was therefore allowed to remain in an exhausted desiccator for several days and then analysed:

0.1109 gave 0.2556  $\text{CO}_2$  and 0.0729  $\text{H}_2\text{O}$ .  $\text{C}=62.86$ ;  $\text{H}=7.30$ .

$\text{C}_{20}\text{H}_{28}\text{O}_7$  requires  $\text{C}=63.2$ ;  $\text{H}=7.4$  per cent.

The figures quoted are those for one of three closely agreeing analyses. They indicate that a partial conversion into the methyl diethyl ester has taken place:

$\text{C}_{19}\text{H}_{26}\text{O}_7$  requires  $\text{C}=62.2$ ;  $\text{H}=7.0$  per cent.

This is perhaps a natural result of the use of a large excess of methyl iodide in the preparation.

*trans-Lactonic Acid of  $\gamma$ -Hydroxy- $\beta$ -cyclohexyl- $\alpha$ -methyltricarballic Acid* (XXXIV, p. 342).

Twenty-five grams of the methylated ester were boiled under a reflux condenser with 170 c.c. of 4*N*-alcoholic potassium hydroxide for two and a-half hours. The mixture was then cooled and the precipitated salts were collected and drained on porous porcelain in a desiccator. They were then dissolved in water and the solution was acidified and repeatedly extracted with ether. The residue left after drying and evaporating the extract was caused to deposit crystals by triturating with benzene, the process being repeated until an ultimate gummy residue was obtained, from which no crystals would separate.



The crystals were placed in a test-tube with just sufficient benzene to cover them. The benzene was then boiled for a few minutes and the suspension filtered while hot. The filtrate on cooling deposited crystals of the lactonic acid.

The ultimate gummy residue was esterified with alcohol and sulphuric acid in the usual way, and, after adding water, the esters were extracted with ether. From the extract the acid products were shaken out with aqueous sodium hydroxide, and again extracted from the aqueous solution after acidification. The residue obtained on evaporating the ether was hydrolysed by boiling hydrochloric acid. After twelve hours the liquid was rendered alkaline and extracted with ether, then re-acidified, and again extracted with ether. On drying and evaporating the latter extract a residue was obtained which, when treated with benzene, yielded a further quantity of the crystalline lactonic acid.

The substance, after recrystallisation from benzene, melted at  $172^{\circ}$  without decomposition, and did not appear to decompose appreciably at  $260^{\circ}$ . It dissolved very readily in water or alcohol, and fairly readily in benzene or chloroform:

0.1310 gave 0.2774  $\text{CO}_2$  and 0.0800  $\text{H}_2\text{O}$ .  $\text{C}=57.75$ ;  $\text{H}=6.78$ .

$\text{C}_{13}\text{H}_{18}\text{O}_6$  requires  $\text{C}=57.8$ ;  $\text{H}=6.7$  per cent.

The silver salt was at once precipitated when silver nitrate was added to a boiled solution of the lactonic acid in ammonia:

0.1118 gave 0.0449 Ag.  $\text{Ag}=44.63$ .

$\text{C}_{13}\text{H}_{16}\text{O}_6\text{Ag}_2$  requires  $\text{Ag}=44.6$  per cent.

*trans-γ-Hydroxy-β-cyclohexyl-α-methyltricarballic Acid.*

The hydroxy-acid appeared to be stable only in the form of its salts, and in spite of several attempts it was not found possible to obtain it free. However, when the *trans*-lactonic acid was dissolved in water and slowly titrated with barium hydroxide an end-point corresponding with the neutralisation of three carboxyl groups was obtained:

0.0434 of the *trans*-lactonic acid required 19.90 c.c.  $\text{Ba}(\text{OH})_2$  solution (0.0243N) for complete neutralisation.  $\text{C}_{13}\text{H}_{18}\text{O}_6$  changing in solution to  $\text{C}_{13}\text{H}_{20}\text{O}_7$  (tribasic) requires 19.85 c.c.

The barium salt was prepared by treating a solution of the *trans*-lactonic acid in water with an excess of aqueous barium hydroxide:

0.1671 gave 0.1202  $\text{BaSO}_4$ .  $\text{Ba}=42.34$ .

$(\text{C}_{13}\text{H}_{17}\text{O}_7)_2\text{Ba}_3$  requires  $\text{Ba}=42.0$  per cent.

*cis-Lactonic Acid of  $\gamma$ -Hydroxy- $\beta$ -cyclohexyl- $\alpha$ -methyltricarballic Acid (XXXIV, p. 342).*

This substance was readily obtained by dissolving its anhydride (see below) in boiling sodium hydroxide solution, and acidifying with hydrochloric acid. Microscopic crystals separated and were recrystallised from water.

The *cis*-lactonic acid melted at  $152^{\circ}$  with the immediate elimination of water vapour. It was more readily soluble in water than the *trans*-acid:

0.1182 gave 0.2489  $\text{CO}_2$  and 0.0724  $\text{H}_2\text{O}$ .  $\text{C}=57.43$ ;  $\text{H}=6.81$ .

$\text{C}_{13}\text{H}_{18}\text{O}_6$  requires  $\text{C}=57.8$ ;  $\text{H}=6.7$  per cent.

The *silver* salt was prepared by adding a solution of silver nitrate to a boiled solution of the *cis*-lactonic acid in ammonia:

0.1029 gave 0.0457 Ag.  $\text{Ag}=44.41$ .

$\text{C}_{13}\text{H}_{18}\text{O}_6\text{Ag}_2$  requires  $\text{Ag}=44.6$  per cent.

On boiling with concentrated hydrochloric acid the *cis*-lactonic acid was partly converted into the *trans*-isomeride.

*cis- $\gamma$ -Hydroxy- $\beta$ -cyclohexyl- $\alpha$ -methyltricarballic Acid.*

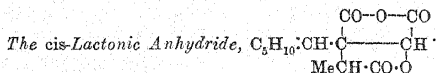
Like the *trans*-modification, this substance appeared to be stable only in the form of its salts. The *cis*-lactonic acid on titration with aqueous barium hydroxide gave, however, an end-point corresponding with salt-formation in respect of three carboxyl groups:

0.0260 of the *cis*-lactonic acid required 11.9 c.c.  $\text{Ba}(\text{OH})_2$  solution (0.0243*N*) for complete neutralisation.  $\text{C}_{13}\text{H}_{18}\text{O}_6$  changing in solution to  $\text{C}_{13}\text{H}_{20}\text{O}_7$  (tribasic) requires 11.9 c.c.

The *barium* salt was precipitated from a solution of the *cis*-lactonic acid in water by the addition of an excess of barium hydroxide solution:

0.1403 gave 0.1011  $\text{BaSO}_4$ .  $\text{Ba}=42.42$ .

$(\text{C}_{13}\text{H}_{17}\text{O}_7)_2\text{Ba}_3$  requires  $\text{Ba}=42.0$  per cent.



The lactonic anhydride was prepared by heating the *trans*-lactonic acid with acetyl chloride at  $100^{\circ}$  in a closed flask. The product was evaporated in a vacuum and the residue crystallised from ether,

when it separated in small crystals melting at  $170^{\circ}$ . It could also be purified by distillation under diminished pressure.

The same anhydride was also obtained by boiling the *cis*-lactonic acid with acetyl chloride at atmospheric pressure:

0.1170 gave 0.2637  $\text{CO}_2$  and 0.0679  $\text{H}_2\text{O}$ .  $\text{C}=61.47$ ;  $\text{H}=6.45$ .

$\text{C}_{13}\text{H}_{16}\text{O}_5$  requires  $\text{C}=61.9$ ;  $\text{H}=6.3$  per cent.

*trans*-3-Hydroxy-4-cyclohexyl-1-methylcyclobutan-2-one-  
3:4-dicarboxylic Acid (XXXVII, p. 345).

The portion of the crystalline mixture obtained in the preparation of the *trans*-lactonic acid (p. 369) which did not dissolve in the boiling benzene consisted essentially of the *cyclobutane* acid XXXVII, and was recrystallised from aqueous alcohol.

The ethereal solution of the esterified gummy residue (p. 369), after shaking out the acid products with aqueous sodium hydroxide, was dried and evaporated. The residue, on distillation under diminished pressure, yielded a fraction passing over at about  $260^{\circ}/25$  mm., which was hydrolysed by boiling hydrochloric acid. The product was rendered alkaline and extracted with ether, then acidified, and again extracted with ether. The latter extract, on drying, and evaporating the solvent, yielded a residue which deposited crystals of the *cyclobutane* acid on adding benzene. The crystals were washed with benzene and recrystallised from aqueous alcohol.

The *trans*-*cyclobutane* acid melted and evolved steam at  $185^{\circ}$ , without appreciable discoloration. The liquid, on cooling, solidified, and on re-heating melted at about  $140^{\circ}$ :

0.1008 gave 0.2132  $\text{CO}_2$  and 0.0618  $\text{H}_2\text{O}$ .  $\text{C}=57.68$ ;  $\text{H}=6.81$ .

$\text{C}_{13}\text{H}_{18}\text{O}_6$  requires  $\text{C}=57.8$ ;  $\text{H}=6.7$  per cent.

0.0600 required 18.37 c.c.  $\text{Ba}(\text{OH})_2$  solution (0.0243*N*) for neutralisation.  $\text{C}_{13}\text{H}_{18}\text{O}_6$  (dibasic) requires 18.3 c.c.

*cis*-3-Hydroxy-4-cyclohexyl-1-methylcyclobutan-2-one-  
3:4-dicarboxylic Acid (XXXVII, p. 345).

The *cis*-acid was prepared by boiling its anhydride (see below) with water. On cooling the solution the anhydride separated in the pure condition.

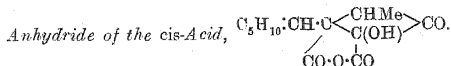
The acid melted at  $148^{\circ}$  with the immediate elimination of water-vapour. It was more readily soluble in water than the *trans*-modification:

0.0704 gave 0.1497  $\text{CO}_2$  and 0.0430  $\text{H}_2\text{O}$ .  $\text{C}=57.99$ ;  $\text{H}=6.78$ .

$\text{C}_{13}\text{H}_{18}\text{O}_6$  requires  $\text{C}=57.8$ ;  $\text{H}=6.7$  per cent.

0.0481 required 14.65 c.c.  $\text{Ba}(\text{OH})_2$  solution (0.0243*N*) for neutralisation.  $\text{C}_{13}\text{H}_{18}\text{O}_6$  (dibasic) requires 14.7 c.c.

When boiled for four hours with concentrated hydrochloric acid the *cis*-acid was quantitatively converted into the *trans*-isomeric acid.



At its melting point the *trans*-acid evolved water-vapour, but the elimination was by no means complete at this temperature. The melted substance was therefore raised to  $230^\circ$  and maintained at this temperature until it began to darken in colour. The product was triturated with aqueous sodium hydrogen carbonate, dried, and recrystallised from dry ether. It melted at  $158^\circ$ .

The same anhydride was obtained by heating the *cis*-acid above its melting point:

0.0833 gave 0.1886  $\text{CO}_2$  and 0.0483  $\text{H}_2\text{O}$ .  $\text{C}=61.75$ ;  $\text{H}=6.44$ .

$\text{C}_{13}\text{H}_{16}\text{O}_5$  requires  $\text{C}=61.9$ ;  $\text{H}=6.3$  per cent.

(g) *Reduction of the Monobasic Bridged-spiro-acid (XXIII, p. 335) by Sodium Amalgam.*

It was found necessary, in order to be able to repeat the results, to standardise carefully the method of experiment. The reductions were always carried out with 3 per cent. amalgam, which passed through a 10-mesh sieve but not through a 16-mesh sieve. The solutions were contained in round-bottomed flasks of capacity two and a-half times the volume of the solution, and kept at a definite temperature. During a reduction a stream of carbon dioxide was led into the flask, but was not allowed to bubble through the liquid. These conditions apply to all the experiments described in this and the next section.

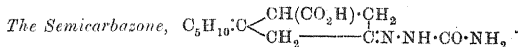
5-cycloHexanespirocyclopentan-3-one-1-carboxylic Acid (XLIII, p. 348).

Five grams of the ketonic acid (XXIII, p. 335) were dissolved in an amount of sodium carbonate sufficient to give a neutral solution and the whole made up to 200 c.c. This solution was kept at  $14^\circ$  by immersing it in cold water and reduced under the standard

conditions by adding 10 grams of amalgam once every half hour until 120 grams in all had been used. Half an hour after the addition of the last of the amalgam the mercurial layer was removed and the aqueous layer acidified. The oily precipitate was allowed to solidify and was then collected and recrystallised from dilute alcohol.

The acid melted at 136—138°, and was found to be very readily soluble in all usual organic solvents except light petroleum; in this solvent, as in water, it was sparingly soluble:

0.0867 gave 0.2145 CO<sub>2</sub> and 0.0635 H<sub>2</sub>O. C=67.49; H=8.14.  
C<sub>11</sub>H<sub>16</sub>O<sub>3</sub> requires C=67.3; H=8.2 per cent.



The semicarbazone separated when a solution in which the acid and semicarbazide acetate had been boiled together was cooled. After recrystallising from alcohol it melted and decomposed at 210°:

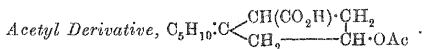
0.1079 gave 0.2262 CO<sub>2</sub> and 0.0757 H<sub>2</sub>O. C=57.17; H=7.80.  
C<sub>12</sub>H<sub>19</sub>O<sub>3</sub>N<sub>3</sub> requires C=56.9; H=7.5 per cent.

5-cycloHexanespirocyclopentan-3-ol-1-carboxylic Acid (XLIV,  
p. 348).

Five grams of the above cyclopentanone acid were dissolved in a quantity of aqueous sodium carbonate sufficient to give an approximately neutral solution which was made up to 400 c.c. This solution was kept at 17° and reduced under standard conditions with 240 grams of amalgam, 10 grams being added every half hour. Half an hour after the addition of the last of the amalgam the mercurial layer was run off and the aqueous layer acidified and extracted with ether. The solid residue obtained after the ether had been dried and distilled off was recrystallised from a mixture of benzene and light petroleum.

The hydroxy-acid melted at 125—127° and was very readily soluble in all the usual organic solvents except light petroleum. It was much more readily soluble in water than was the corresponding ketonic acid:

0.1092 gave 0.2672 CO<sub>2</sub> and 0.0884 H<sub>2</sub>O. C=66.93; H=9.00.  
C<sub>11</sub>H<sub>18</sub>O<sub>3</sub> requires C=66.7; H=9.1 per cent.



When the hydroxy-acid was boiled with acetyl chloride for four hours and the solution evaporated there was left a solid residue which was recrystallised from benzene. It melted at 157—160°:

0·0887 gave 0·2122  $CO_2$  and 0·0680  $H_2O$ .  $C=65\cdot24$ ;  $H=8\cdot52$ .

$C_{13}H_{20}O_4$  requires  $C=65\cdot0$ ;  $H=8\cdot3$  per cent.

0·1552 gave acetic acid requiring 26·4 c.c.  $Ba(OH)_2$  solution (0·0243*N*) for neutralisation.  $C_{13}H_{20}O_4$  requires 26·6 c.c.

(h) *Comparative Experiments on the Reduction of the Bridged-ring- and Bridged-spiro-acids XIV (p. 333) and XXIII (p. 335).*

The general plan which was followed in these experiments has already been sketched in the Introduction (Section E).

The most convenient method of preparing the bridged-ring acid XIV was found to be by treating the sodium compound IX (p. 330) according to the method (p. 364) used in the preparation of the acid XXIII from the sodium compound XII. The reductions of the bridged-ketonic-acids XIV and XXIII were carried out under the usual conditions (p. 372). The experiments were conducted in pairs, using 0·80 gram of the acid XIV and 1·00 gram of the acid XXIII. The neutral solutions of the acids were immersed in the same water-bath and treated with 1 gram of amalgam every fifteen minutes so long as the experiment lasted. The aqueous layers were then acidified and extracted quantitatively with pure ether. The solid residues obtained on evaporating the solvent were allowed to remain in an exhausted desiccator for forty-eight hours.

The dried products were then analysed. Usually about 0·4 or 0·5 gram was taken and the water formed by combustion determined. In certain cases the substance was also acetylated and the product left after evaporating, desiccated over potassium hydroxide and quantitatively hydrolysed, the acetic acid being distilled off in a current of steam and estimated by titration with standard alkali. This figure gave the quantity of hydroxy-acid which had been formed in the reduction, whilst the water formed on combustion enabled one to calculate the total quantity of hydrogen which had been introduced during the reduction. The accompanying table (table VII) gives the results of these experiments, the figures within the brackets (.....) representing the calculated limits.

Another set of experiments, similar to the above, was instituted,

in which the reduced ketonic-acids XXXIX (p. 346) and XLIII (p. 348) were used in place of the bridged-ketonic-acids XIV and XXIII. The quantities taken for each experiment were 0.80 gram of the acid XXXIX, and 1.00 gram of the *spiro*-acid XLIII. The other quantities and conditions of experiment were the same as in the former case. In this instance the products were not acetylated and hydrolysed, but the water formed on combustion was determined. The results of these experiments are given in table VIII, the figures in brackets (.....) representing, as before, the calculated limits.

TABLE VII.

Time (hours).	Amalgam (grams).	Bridged-ring-acid (0.80 gram).			Bridged- <i>spiro</i> -acid (1.00 gram).		
		Per cent. of H in product.	Atoms of H introduced.	Per cent. hydroxy- acid.	Per cent. of H in product.	Atoms of H introduced.	Per cent. hydroxy- acid.
(0	0	6.49	0.00	0	7.22	0.00	0)
1	4	6.67	0.30	—	7.49	0.58	—
2	8	6.85	0.60	—	7.64	0.89	—
4	16	7.20	1.18	—	7.97	1.58	—
6	24	7.27	1.30	0	8.09	1.85	3
10	40	7.46	1.62	3	8.30	2.30	18
14	56	7.79	2.16	21	—	—	—
(∞	∞	8.86	4.00	100	9.09	4.00	100)

TABLE VIII.

Time (hours).	Amalgam (grams).	Ring-acid (0.80 gram).		<i>spiro</i> -Acid (1.00 gram).	
		Per cent. of H in product.	Atoms of H introduced.	Per cent. of H in product.	Atoms of H introduced.
(0	0	7.69	0.00	8.16	0.00)
2	8	7.92	0.39	8.39	0.49
4	16	8.13	0.75	8.51	0.75
7	28	8.42	1.25	8.67	1.10
(∞	∞	8.86	2.00	9.09	2.00)

(i) *Oxidation of Fission-products Derived from the Bridged-*spiro*-sodio-ester XII (p. 330).*

Oxidation experiments were tried with three types of fission-product, including the *spiro*cyclopentanone acid XLIII (p. 348), the *trans*cyclohexylcyclobutane acid XXIV (p. 336), and the *trans*-lactonic acid of hydroxycyclohexylmethyltricarballic acid XXXIV (p. 342). None of these appeared to be acted on by boiling dilute nitric acid. Concentrated nitric acid, however,

readily oxidised the first of these three acids, but did not react with the last two. These, however, were readily attacked by warm alkaline permanganate. Two crystalline oxidation products, *cyclohexanecarboxylic acid* and *cyclohexane-1:1-dicarboxylic acid*, were obtained in the course of these experiments.

*cycloHexane-1:1-dicarboxylic Acid* (XLV, p. 351).

This acid was prepared by oxidising both the *spirocyclopentanone acid* XLIII (p. 348), or the corresponding *spirocyclopentanol acid* XLIV (p. 348), with concentrated nitric acid. The organic acid (2.5 grams) was warmed with an excess of concentrated nitric acid until most of the red fumes had been evolved. The resulting solution was then boiled for a few minutes, and finally evaporated to dryness. The residue was treated with water and again evaporated. In this way, a semi-solid mass was obtained, from which the crystals were separated by spreading on porous porcelain.

After recrystallising from water, the acid melted at  $207^{\circ}$ , with the evolution of carbon dioxide and a certain amount of discoloration:

0.1008 gave 0.2058  $\text{CO}_2$  and 0.0650  $\text{H}_2\text{O}$ . C=55.68; H=7.16.

$\text{C}_8\text{H}_{12}\text{O}_4$  requires C=55.8; H=7.0 per cent.

0.0412 required 19.75 c.c.  $\text{Ba}(\text{OH})_2$  solution (0.0243*N*) for neutralisation.  $\text{C}_8\text{H}_{12}\text{O}_4$  (dibasic) requires 19.7 c.c.

*cycloHexanecarboxylic Acid* (*Hexahydrobenzoic Acid*).

This acid was obtained in two ways:

(1) *By distilling cyclohexane-1:1-dicarboxylic acid.* The dicarboxylic acid on distillation under ordinary pressure gave off carbon dioxide and yielded a distillate, which boiled at  $230\text{--}235^{\circ}$  and solidified when cooled by ice. The crystals melted at  $18\text{--}23^{\circ}$ . (Found: C=65.42; H=9.51. Calc.: C=65.6; H=9.4 per cent.)

(2) *By oxidising cyclohexyl derivatives.* Either the *trans-lactonic acid* of *hydroxycyclohexylmethyltricarballic acid* XXXIV (p. 342) or the *trans-cyclohexylcyclobutanone acid* XXIV (p. 336) may be used. The organic acid (10 grams) was dissolved in an excess of a solution of sodium carbonate and treated with 30 grams of potassium permanganate. The permanganate was added in successive small quantities, sufficient time being allowed between each addition for the solution to become decolorised, the reaction being aided by heating. When all the permanganate had



been added and decolorised, the liquid was filtered and extracted with ether to remove any neutral oxidation products. The aqueous solution was then acidified with hydrochloric acid, and the acid products were extracted with ether. From the residue obtained on drying and evaporating the solvent, some gummy material was separated by distilling under diminished pressure, and the liquid distillate was fractionally distilled under atmospheric pressure. In this way, there was obtained a fraction boiling at 232—236°, which solidified on cooling in ice to a mass of crystals melting at 21—25°. (Found: C=65·63; H=9·51. Calc.: C=65·6; H=9·4 per cent.)

The acid prepared by both these methods melted at a temperature a few degrees lower than the recorded melting point, namely, 29° (Lumsden, T., 1905, 87, 91). The same experience in regard to it is recorded by Haworth and Perkin (T., 1894, 65, 103). It certainly appears to be exceedingly difficult to obtain preparations showing the correct melting point when working with small quantities of material. Crystals of the acid when left exposed to air rapidly liquefied, and it did not appear to be possible to induce the acid to separate in a crystalline form by cooling a solution in light petroleum below 0°. These observations agree precisely with the statements made by Lumsden, and, along with the analytical figures, are regarded as leaving no doubt as to the identity of the substance.

(j) *Examination of the Oily By-product obtained in the Preparation of the Bridged-spiro-sodio-ester XII* (p. 330).

The alcoholic solution of the oily by-product obtained during the preparation of the yellow sodium spiro-compound (p. 357) was distilled to remove the alcohol, the residue dissolved in ether and shaken with water. The ethereal solution was then dried and evaporated, the residue being distilled under diminished pressure. Three fractions were obtained: (1) below 120°/20 mm., (2) between this and 250°/11 mm., and (3) at 250—160°/11 mm., together with a small, dark-coloured, non-volatile residue.

*Fraction (1).*—The first fraction contained practically the whole of the ethyl malonate present in the original oil. It was redistilled, and the small residue of high boiling point was added to the second fraction, (2).

*Fraction (2).*—The second fraction, which did not appear to be capable of separation into pure compounds by distillation, was boiled with hydrochloric acid for forty-eight hours. During the reaction, a strong odour of butyric acid was developed. When

the hydrolysis was complete, the butyric acid was distilled off in a current of steam, and the residual solution boiled with charcoal, filtered, and evaporated to dryness. Five acids were isolated from the crystalline residue.

*cycloHexane-1:1-diacetic Acid*.—The crystalline residue was recrystallised from the minimal quantity of 35 per cent. alcohol. The crystals which separated contained three of the five acids, the separation from the other two, which remained in the mother liquor, being very nearly quantitative. The crystals melted at 160—200° approximately. They were dissolved in dilute ammonia and, after the excess of ammonia had been evaporated, were treated in the cold with a solution of zinc sulphate. The precipitate was collected, washed with cold water, and then digested with hydrochloric acid. The acid thus precipitated melted at 174—179°, and was again precipitated as its zinc salt. The free acid was then liberated and recrystallised from water, when it melted at 181°, and was identified as *cyclohexane-1:1-dicarboxylic acid* by direct comparison with a specimen of that substance. The preparation, together with some small residues obtained subsequently, constituted 15 per cent. of the original crystalline mixture.

*trans-cycloHexanespirocyclopropane-1:2-dicarboxylic Acid*.

The combined filtrates from the zinc salt of *cyclohexane-1:1-diacetic acid* were concentrated and treated with concentrated hydrochloric acid. The precipitated acids were dissolved in ammonia, and, after concentrating the solution, treated in the cold with a considerable excess of a saturated solution of lead nitrate. The lead salts were collected and recrystallised from the minimal quantity of boiling water, and then decomposed with a slight excess of dilute nitric acid. This treatment separated the last trace of *cyclohexanediactic acid*, which, along with a small quantity of the *trans-spirocyclopropane acid*, remained in the filtrates from the lead salt. These traces were separated by means of their zinc salts, as described above. The combined *cyclohexanediactic acid-free* preparations were extracted twice with three parts by weight of boiling benzene. The undissolved portion melted at 234—237°, and on recrystallisation from dilute alcohol melted sharply at 237°. It was identified as *cyclohexanespirocyclopropanedicarboxylic acid* by direct comparison with a specimen. The preparation, together with some residues subsequently obtained, amounted to 65 per cent. of the original crystalline mixture.

3-cycloHexanespiro-1-methylcyclopropane-1:1':2-tricarboxylic  
Acid (XLVII, p. 354).

The solution in the 35 per cent. alcohol from which the above two dicarboxylic acids were crystallised (p. 378) was evaporated, and the residue resolved by crystallisation from 50 per cent. alcohol into three distinct fractions: (1) a small quantity of a mixture of the same two dicarboxylic acids, (2) a much more readily soluble, crystalline substance melting at about 208°, and (3) a viscous gum.

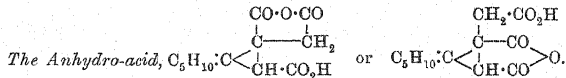
The first fraction was treated according to the methods already described for the separation of the two dicarboxylic acids.

The second consisted essentially of the *spirocyclopropanetricarboxylic acid*. It represented about 8 per cent. of the original crystalline mixture, and, on recrystallising from water, melted at 215°, with the immediate elimination of water vapour:

0.1156 gave 0.2386 CO<sub>2</sub> and 0.0675 H<sub>2</sub>O. C=56.30; H=6.49.

C<sub>12</sub>H<sub>16</sub>O<sub>6</sub> requires C=56.2; H=6.2 per cent.

0.0453 required 21.95 c.c. Ba(OH)<sub>2</sub> solution (0.0243*N*) for neutralisation. C<sub>12</sub>H<sub>16</sub>O<sub>6</sub> (tribasic) requires 21.9 c.c.



The anhydro-acid was prepared by boiling the free tricarboxylic acid with acetyl chloride for two hours and evaporating the excess of the reagent. The residue on treating with benzene set to a mass of crystals. After recrystallising from the same solvent, the anhydro-acid melted at 128°. It was immediately soluble in cold sodium hydrogen carbonate solution, and could be recovered unchanged by acidifying. On boiling a solution of the anhydro-acid in aqueous sodium hydroxide for a few minutes and then acidifying, the free tribasic acid was regenerated:

0.1548 gave 0.3418 CO<sub>2</sub> and 0.0823 H<sub>2</sub>O. C=60.23; H=5.90.

C<sub>12</sub>H<sub>14</sub>O<sub>5</sub> requires C=60.5; H=5.9 per cent.

5-cycloHexanespiro-2-ethylidicyclopentan-3-one-1-carboxylic  
Acid (XLVIII, p. 354).

The two benzene filtrates obtained in the preparation of the *spirocyclopropanedicarboxylic acid* (p. 378) were combined and evaporated. The residue, which still contained about three parts

of the dicarboxylic acid to one of the bridged-monocarboxylic acid (this was indicated by a titration), was weighed, and extracted with three times its weight of boiling benzene. The extract was evaporated and the residue treated again in this way, the treatment being repeated until the residue obtained after evaporating an extract was completely soluble in three parts of boiling benzene. The product was fractionally crystallised from benzene. After a considerable number of fractional crystallisations, a preparation was obtained which did not appear to change in melting point when again recrystallised.

This substance separated from benzene in long needles, which melted at 191—194°. It was sparingly soluble in water and gave no colour with ferric chloride:

0.0610 gave 0.1537  $\text{CO}_2$  and 0.0432  $\text{H}_2\text{O}$ .  $\text{C}=69.75$ ;  $\text{H}=7.99$ .

$\text{C}_{13}\text{H}_{18}\text{O}_3$  requires  $\text{C}=70.3$ ;  $\text{H}=8.1$  per cent.

0.0376 required 7.20 c.c.  $\text{Ba}(\text{OH})_2$  solution (0.0243*N*) for neutralisation.  $\text{C}_{13}\text{H}_{18}\text{O}_3$  (monobasic) requires 7.0 c.c.

The analytical figures, especially those for the titration, do not correspond with the formula so well as could be desired. The discrepancies are, however, all in a direction that may be taken to indicate that the preparation still contained a small quantity of the *spirocyclopropanedicarboxylic acid*, which, owing to the smallness of the quantity of material, it was not possible to remove. The preparation constituted about 0.1 per cent. of the original crystalline mixture.

*trans-Lactonic Acid of  $\gamma$ -Hydroxy- $\beta$ -cyclohexyl- $\alpha$ -ethyltricarballic Acid (XLIX, p. 354).*

The viscous gum, which was obtained as the third fraction in the separation by means of 50 per cent. alcohol mentioned on p. 379, was distilled under diminished pressure. More than three-quarters of it passed over at 240—250°/40 mm., and this, on treatment with benzene, solidified to a mass of colourless crystals. These represented about 3 per cent. of the original crystalline mixture, the residue in the distilling flask, which was not further examined, accounting for about 1 per cent.

The crystalline lactonic acid, after recrystallisation from either water or benzene, melted at 149°. It dissolved readily in water and all the usual organic solvents except light petroleum:

0.1228 gave 0.2660  $\text{CO}_2$  and 0.0962  $\text{H}_2\text{O}$ .  $\text{C}=59.08$ ;  $\text{H}=7.09$ .

$\text{C}_{14}\text{H}_{20}\text{O}_6$  requires  $\text{C}=59.2$ ;  $\text{H}=7.0$  per cent.

The silver salt was precipitated by adding silver nitrate solution to a boiled solution of the lactonic acid in ammonia:

0.1063 gave 0.0461 Ag.  $\text{Ag}=43.37$ .

$\text{C}_{14}\text{H}_{18}\text{O}_6\text{Ag}_2$  requires  $\text{Ag}=43.4$  per cent.

*trans-γ-Hydroxy-β-cyclohexyl-α-ethyltricarballic Acid.*

This hydroxy-acid (contrast the *cis*-form) appeared to be stable only in the form of its salts. All attempts to obtain it in the free state were unsuccessful. However, when the *trans*-lactonic acid was dissolved in water and the solution titrated slowly with barium hydroxide in the cold, an end-point corresponding with the neutralisation of three carboxyl groups was obtained:

0.0516 required 22.40 c.c.  $\text{Ba}(\text{OH})_2$  solution (0.0243*N*) for complete neutralisation.  $\text{C}_{14}\text{H}_{20}\text{O}_6$ , changing in solution to  $\text{C}_{14}\text{H}_{22}\text{O}_7$  (tribasic), requires 22.4 c.c.

The *barium* salt was precipitated from an aqueous solution of the *trans*-lactonic acid by adding an excess of a solution of barium hydroxide:

0.1678 gave 0.1179  $\text{BaSO}_4$ .  $\text{Ba}=41.36$ .

$(\text{C}_{14}\text{H}_{19}\text{O}_7)_2\text{Ba}_3$  requires  $\text{Ba}=40.8$  per cent.

*cis-Lactonic Acid of γ-Hydroxy-β-cyclohexyl-α-ethyltricarballic Acid (XLIX, p. 354).*

The *cis*-lactonic acid was readily prepared by heating the free *cis*-hydroxy-acid (see below) at  $100^\circ$  for a few minutes.

When dissolved in water the lactonic acid regenerated the hydroxy-acid, which could either be crystallised out or titrated in solution. The lactonic acid could, however, be recrystallised from a mixture of benzene and light petroleum without any change taking place. It melted at  $198^\circ$  with the evolution of water-vapour:

0.1040 gave 0.2244  $\text{CO}_2$  and 0.0664  $\text{H}_2\text{O}$ .  $\text{C}=58.84$ ;  $\text{H}=7.10$ .

$\text{C}_{14}\text{H}_{20}\text{O}_6$  requires  $\text{C}=59.2$ ;  $\text{H}=7.0$  per cent.

The *silver* salt was prepared by dissolving either the *cis*-lactonic acid or the *cis*-hydroxy-acid (see below) in dilute ammonia, boiling, and adding an excess of silver nitrate solution:

0.1041 gave 0.0449 Ag.  $\text{Ag}=43.13$ .

$\text{C}_{14}\text{H}_{18}\text{O}_6\text{Ag}_2$  requires  $\text{Ag}=43.4$  per cent.

On boiling the *cis*-lactonic acid with hydrochloric acid a partial conversion into the *trans*-lactonic acid took place.

*cis-γ-Hydroxy-β-cyclohexyl-α-ethyltricarballic Acid.*

This substance was prepared by boiling the *cis*-lactonic anhydride (see below) with a slight excess of aqueous sodium hydroxide and acidifying with hydrochloric acid. The *cis*-hydroxy-acid slowly separated out.

The substance is very unstable, and loses a molecule of water with great readiness, giving the *cis*-lactonic acid. The change was found to proceed with rapidity at 60° in an exhausted desiccator at the ordinary temperature, and slowly when the acid was exposed to air under ordinary conditions. In cold aqueous solution the substance behaved in every way as a tribasic acid:

0.1003 gave 0.2045 CO<sub>2</sub> and 0.0666 H<sub>2</sub>O. C=55.60; H=7.38.

C<sub>14</sub>H<sub>22</sub>O<sub>7</sub> requires C=55.6; H=7.3 per cent.

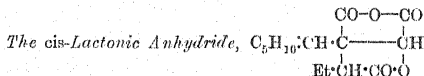
0.0382 required 16.65 c.c. Ba(OH)<sub>2</sub> solution (0.0243*N*) for neutralisation. C<sub>14</sub>H<sub>22</sub>O<sub>7</sub> requires (tribasic) 16.6 c.c.

The *barium* salt was precipitated when the hydroxy-acid was dissolved in water and treated with an excess of barium hydroxide solution:

0.1057 gave 0.0740 BaSO<sub>4</sub>. Ba=41.18.

(C<sub>14</sub>H<sub>18</sub>O<sub>7</sub>)<sub>2</sub>Ba<sub>3</sub> requires Ba=40.8 per cent.

When the *cis*-hydroxy-acid was boiled with 20 per cent. hydrochloric acid for some hours a partial conversion into the *trans*-lactonic acid took place.



The *trans*-lactonic acid did not appear to be dehydrated to any appreciable extent when heated above its melting point or when distilled under diminished pressure. It readily eliminated water, however, when heated at 100° for half an hour with acetyl chloride. On evaporating the product and treating the residue with benzene, crystals of the lactonic anhydride were obtained. After being recrystallised from benzene the substance melted at 154°. It did not dissolve at an appreciable rate in cold aqueous sodium hydrogen carbonate, but on warming with sodium hydroxide both oxygen rings were opened up and the *cis*-hydroxy-acid was formed:

0.1023 gave 0.2356 CO<sub>2</sub> and 0.0625 H<sub>2</sub>O. C=62.81; H=6.79.

C<sub>14</sub>H<sub>18</sub>O<sub>5</sub> requires C=63.2; H=6.7 per cent.

*Fraction (3).*—The third fraction which was obtained on distilling

the oily by-product (p. 377) boiled at 250—260°/11 mm. and consisted of fairly pure ethyl *cyclohexanespiromethylcyclopropanetetracarboxylate* (XI, p. 330). When hydrolysed with hydrochloric acid it yielded the tricarboxylic acid (XLVII, p. 354) dealt with on p. 379.

(k) *Note on Ethyl Dihydrogen 5:5-Dimethyldicyclopentan-3-one-1:2:4-tricarboxylate* (XXVI, p. 337).

This member of the dimethyldicyclopentane series, which was made use of in this research, has not been previously described.

The yellow sodium compound X (p. 330) was boiled with five times its weight of a 3*N*-solution of potassium hydroxide in alcohol until the suspended matter just became colourless. The precipitate was collected and drained on porous porcelain in a desiccator. It was then dissolved in the minimal quantity of water and decomposed with excess of concentrated hydrochloric acid. The crystals obtained were recrystallised from 15 per cent. hydrochloric acid.

The acid-ester melted and decomposed at 162°, and gave a purple colour with ferric chloride. It was readily converted into the monocarboxylic acid XIV (p. 333) by heating for a few minutes at 200° with a little water. When heated in the dry state, it evolved carbon dioxide and steam, and from the charred residue a small amount of the acid XIV was isolated. It is perhaps worthy of note that the monocarboxylic acid should be obtained in this way, but it is doubtless the result of the hydrolytic action of the steam which is evolved as the substance decomposes:

0.1261 gave 0.2453 CO<sub>2</sub> and 0.0599 H<sub>2</sub>O. C=53.05; H=5.28.

C<sub>12</sub>H<sub>14</sub>O<sub>7</sub> requires C=53.3; H=5.2 per cent.

0.1070 required 32.7 c.c. Ba(OH)<sub>2</sub> solution (0.0243*N*) for neutralisation. C<sub>12</sub>H<sub>14</sub>O<sub>7</sub> (dibasic) requires 32.6 c.c.

IMPERIAL COLLEGE OF SCIENCE  
AND TECHNOLOGY,  
SOUTH KENSINGTON.

RESEARCH LABORATORIES,  
CASSEL CYANIDE COMPANY, LTD.,  
GLASGOW.

[Received, March 13th, 1919.]

# ANNUAL GENERAL MEETING,

THURSDAY, MARCH 27TH, 1919, AT 4 P.M.

SIR WILLIAM J. POPE, K.B.E., F.R.S., President, in the Chair.

Dr. T. S. PRICE and Dr. C. K. TINKLER were elected Scrutators, and the ballot was opened for the election of Officers and Council.

The Report of Council for 1917-1918 was formally presented to the meeting by the PRESIDENT. After statements by one of the Secretaries as to the progress made in the revision of the Bye-laws and by the Treasurer as to the financial position of the Society, the adoption of the Report of Council, together with the Statement of Accounts for the year ending December 31st, 1918, was proposed by Professor G. BARGER, seconded by Dr. G. W. MONIER-WILLIAMS, and carried unanimously.

## REPORT OF COUNCIL, 1918-1919.

The Council are gratified to report a substantial increase in the membership of the Society. On December 31st, 1917, the number of Fellows was 3,270. During 1918, 249 Fellows were elected and 13 reinstated, making a gross total of 3,532. The Society has lost 62 Fellows by death; 16 have resigned; the elections of 6 have been declared void, and 47 have been removed for non-payment of Annual Subscriptions. The total number of Fellows, therefore, as at December 31st, 1918, was 3,401, showing an increase of 131, as compared with 72 in 1917.

It is with regret they report that the following Fellows have died on Service:

John Percy Bates (1913).  
Charles William Dick (1917).

Edward Frank Harrison (1894).  
Leonard Ison Pitt (1911).



and that the death of the following has also occurred:

Richard Leburn Barnes (1875).	Thomas Stratford Logan (1902).
James Bayne (1874).	Thomas Watson Lovibond (1882).
William Henry Blake (1890).	Sydney Lupton (1872).
Arthur Clegg Bowdler (1865).	George Cannon McMurtry (1889).
Joseph John Bowley (1896).	Charles Stewart Maries (1918).
Harry Broadbent (1889).	Edward Matthey (1884).
William Edward Callister (1909).	Elias Mendoza (1918).
Thomas Charles Cloud (1878).	Alexander Milne (1885).
James Mason Crafts (1870).	Sir Alexander Pedler (1870).
William Adam Dixon (1862).	Mulgrave Daniel Penney (1870).
John Ernest Dunstan (1917).	George Frederick Tyler Phillips (1904).
Thomas Farries (1870).	William Ping (1889).
Charles Thomas Foreman (1907).	Joseph Price Remington (1886).
Edward Francis (1879).	Alfred Gordon Salamon (1880).
Charles James Pemeller Fuller (1896).	John Scudamore Sellon (1875).
George Thomas Glover (1872).	Alfred Senier (1875).
Walter Augustus Handcock (1900).	Walter Dalrymple Severn (1896).
Egerton Hargreaves (1909).	John William Shepherd (1899).
Henry James Helm (1872).	Richard Spencer (1886).
Richard Pendarves Hodges (1913).	James Carter Spensley (1917).
Henry Tylston Hodgson (1873).	Henry Charles Stephens (1880).
William Lamond Howie (1876).	Edward Cumming Thompson (1894).
Edward Lewis James (1912).	John Bishop Tingle (1889).
David Smith Jardin (1902).	Thomas Tyrer (1876).
Edgar Dingle Jones (1912).	Herbert William Mills Willett (1906).
John Sydney Keel (1917).	Christopher Wilson (1894).
Douglas Rayment Keller (1913).	Reginald Cowdell Woodcock (1871).
William Joel Kemp (1882).	John Young (1874).
Hassum Alidina Lakhani (1909).	
Edmund Albert Letts (1879).	

#### Resignations have been received from:

William James Bees (1905).	Frederick Filmer de Morgan (1897).
Hugh Garner Bennett (1909).	Joseph Morris (1891).
Kula Bhushan Bhaduri (1903).	Malur Srinivasa Rau (1910).
Frederick Raine Ennos (1914).	Abhayacharan Sanyal (1891).
Nagardas Purushottam Gandhi (1915).	Robert Greig Smith (1891).
John Thomas Hall (1903).	Thomas May Smith (1910).
Herbert Edwin Macadam (1896).	Alfred Tingle (1904).
David James Morgan (1895).	James Woodward (1888).

The congratulations of the Society are offered to Professor William Odling, Past-President, elected a Fellow on January 17th, 1848, who has now completed seventy-one years as a Fellow. The Society's congratulations are also extended to:

	Elected.
Dr. Augustus George Vernon Harcourt (Past-President).....	Feb. 3rd, 1859.
John Spiller .....	Feb. 3rd, 1859.
Josiah Wyckliffe Kynaston.....	Feb. 17th, 1859.
Thomas William Salter.....	Feb. 17th, 1859.

who have been Fellows for more than sixty years, and to the following, who have attained their jubilee as Fellows:

	Elected.
John Hughes .....	Dec. 17th, 1868.
Edward Knowles Muspratt.....	Jan. 21st, 1869.
Thomas Bolas .....	Mar. 18th, 1869.
Frank Clowes .....	Mar. 18th, 1869.

The volume of Transactions for 1918 contains 995 pages, of which 849 pages are occupied by 89 memoirs, the remaining 146 pages being devoted to the Obituary Notices, three lectures on special subjects, the Report of the Annual General Meeting, and the Presidential Address. The volume for the preceding year contained 95 memoirs occupying 960 pages. The Journal for 1918 contains also 2,436 abstracts occupying 1,032 pages, whilst the abstracts for 1917 numbered 2,858 and occupied 1,308 pages. The great decrease in the number of memoirs in journals devoted to chemistry and allied subjects referred to in the Reports for 1916 and 1917 became, as was expected, still more marked in 1918; there is, however, some slight reason to hope that the lowest point has been reached, and that an increase in the number of papers abstracted may now be anticipated. Whilst most of the Continental journals have been obtained for abstraction, no Russian journals have come to hand during the year.

In the last Report, an account was given of the arrangements made by a Joint Committee of the Chemical Society and Society of Chemical Industry to minimise duplication in the abstracts published in the Journals of the two Societies. This arrangement has been in force during the year with satisfactory results.

The abstracts may be classified as follows:

#### PART I.

	Pages.	No. of Abstracts.
Organic Chemistry .....	—	771
Physiological Chemistry .....	—	237
Chemistry of Vegetable Physiology and Agriculture ...	—	160
	564	1,168

#### PART II.

General and Physical Chemistry .....	—	557
Inorganic Chemistry .....	—	205
Mineralogical Chemistry .....	—	59
Analytical Chemistry .....	—	447
	468	1,268
Total in Parts I. and II .....	1,032	2,436

The scheme for supplying the abstracts of the Chemical Society and of the Society of Chemical Industry to the members of both Societies has been further considered, but owing to many difficulties arising out of the war, such as the greatly increased cost of production, it has been postponed for the present.

The Report on the progress of Radioactivity for 1917, which was omitted from the last volume of Annual Reports, is included with that for 1918 in the current Volume XV; it has been decided to postpone the Report on Crystallography and Mineralogy for 1918 and to combine this with the Report for 1919. Permission has been given for the publication of a French translation of Volume XV of the Annual Reports.

The publication of the List of Fellows has been resumed, but, owing to the need for economy, the list has been issued only to those Fellows who made application.

Following the scheme initiated three years ago, arrangements have been made for the delivery of Lectures to the Society during the present session. The first, entitled "The conception of the chemical element as enlarged by the study of radioactive change," was given by Professor F. Soddy on December 19th; on March 6th a lecture on "Emission spectra and atomic structure" was delivered by Professor Nicholson, whilst Professor Jeans will give a lecture on May 1st dealing with "The quantum theory and new theories of atomic structure."

The address delivered by the President at the last Annual Meeting was, by order of the Council, widely circulated throughout the country. The emphasis laid in this address on the desirability of closer co-operation between the societies representing the various branches of chemistry has given rise to a definite step in this direction by the promotion of "The Federal Council for Pure and Applied Chemistry." The Federal Council consists of representatives appointed by the following eleven societies: the Chemical Society, the Society of Chemical Industry, the Association of British Chemical Manufacturers, the Institute of Chemistry, the Society of Public Analysts, the Faraday Society, the Biochemical Society, the Iron and Steel Institute, the Institute of Brewing, the Society of Dyers and Colourists, and the Society of Glass Technology. The delegates elected by the Council to represent the Society on this body are Professor H. E. Armstrong, Sir William J. Pope, and Sir William A. Tilden. The primary objects of the new body are to consider and act upon all matters involving the common interests of the constituent societies and to deal with any question which these may place before it. The provision of a House adequate to the requirements of the chemical profession, in

which a complete scientific and technical Library could be assembled, is now under the consideration of the Federal Council.

The Council have had under consideration the present conditions of chemical research, and they have given particular attention to the question of the adequacy of the sums available for grants and to the restricted supply of pure chemicals. Since it appeared desirable that united action should be taken in these matters, the Federal Council has been requested to consider them, and has already taken action in both directions.

The demobilisation of chemists has also had the earnest attention of the Council, and joint representation with the Royal Society, the Institute of Chemistry, and the Chemical Warfare Department has been made to the proper authorities.

The Council have recently received a valuable report from the General Committee of Chemical and Allied Societies on the proposed publication of chemical compendia in the English language. The report has also been placed before the Federal Council and the councils of other interested societies, including those of the American and French Chemical Societies, with the view of securing their co-operation.

During the past year a Committee has been appointed to consider what changes it is desirable to make in the Bye-laws of the Society. In their report, the Committee have recommended considerable changes, but these are in several respects inconsistent with the terms of the present Charter, and therefore cannot be made until a supplemental Charter has been obtained. The question whether application for a supplemental Charter should be made will shortly be laid before an Extraordinary General Meeting.

Sir William A. Tilden represented the Society on the Sectional Committee of the British Scientific Products Exhibition.

Professor P. F. Frankland and Dr. A. Scott continue to act as the Society's representatives on the Conjoint Board of Scientific Societies, whilst Sir William J. Pope has been appointed a delegate to the International Association of Chemical Societies in place of the late Sir William Ramsay.

The Council are glad to report that, as a result of the Conference of Chemical and Allied Societies, a scheme has been prepared and is now in operation for increasing the use of the Library and extending its technical equipment. The co-operation and financial assistance of the Association of British Chemical Manufacturers, the Biochemical Society, the Faraday Society, the Institute of Chemistry, the Society of Chemical Industry, the Society of Dyers and Colourists, and the Society of Public Analysts have been obtained. The members of these societies are now able to use the

Library on the same terms as Fellows, and their representatives have been added to the Library Committee.

As already announced, the Library is now open to 9 p.m. on Tuesdays and Fridays and to 5 o'clock on Saturdays, in addition to those evenings on which the Society meets.

The number of books borrowed from the Library during 1918 was 2,905, as against 2,157 in the previous year and 1,610 in 1916. The additions to the Library comprise 126 books, 255 volumes of periodicals, and 31 pamphlets, compared with 155 books, 282 volumes of periodicals, and 54 pamphlets in 1917.

The Council have the pleasure to report that a valuable gift of handsomely bound volumes of periodicals and systematic works has been received as a bequest from the late Mr. Sydney Lupton.

The accounts for the year 1918 show a balance of income over expenditure amounting to £2,489 4s. 4d., as against £1,652 9s. 11d. reported last March for the previous year. Whilst the income from all sources has been £10,082 14s. 11d., and is thus greater than that recorded for 1917 by £1,552 16s. 0d., the expenditure has exceeded that of 1917 by £716 1s. 7d., reaching the sum of £7,593 10s. 7d. Thus, although the increased expenditure exceeds the similar increase on the outlay for 1916, indicated by the Report of last year, it has been amply covered by the larger revenue.

The latter factor is composed of additional life compositions, £102, and admission fees, £352, whilst the subscriptions account reveals an improvement by £381 10s. 0d. To these are added increases of £89 12s. 7d. from interest on investments, £262 9s. 10d. from the sale of publications, and £92 15s. 11d. from advertisements in the Journal, although the net gain to the Society from this source is only £32 5s. 4d., owing to increased cost of printing. Donations to the Library amounting to £280 5s. 0d., and not having a corresponding reference in the Report for 1917, cannot properly be regarded as increased revenue, as more than this sum will be expended by the Society during the current year in augmenting the usefulness of the Library to members of the subscribing bodies.

As was anticipated from the conditions prevailing during 1918, expenses in producing the various publications have been greater than the corresponding costs for 1917, the total increase being £390 19s. 7d., of which £128 5s. 2d. is due to the list of Fellows, a publication suspended in 1917. The fact that this compilation cost £73 1s. 6d. in 1914, £73 6s. 7d. in 1915, and £73 16s. 4d. in 1916 throws an interesting light on the increase in printing charges and on the period of the War at which this became acute.

Administrative expenditure has also increased from £1,472 4s. 5d.

to £1,681 6s. 5d., the principal items on this account being £161 14s. 10d. in staff salaries and war bonus, whilst miscellaneous printing, stationery, and postages have together increased by £85 18s. 8d. On the other hand, the exceptional outlay in library furniture required in 1917 has not been repeated, and is reflected in a saving of £61 9s. 9d. in the year under review.

The War has continued to affect the volume of Transactions and Abstracts, as indicated by the following synopsis:

				Number of Pages.		
				Trans.	Abstr.	Total.
1914	...	...	...	2,909	2,068	4,977
1915	...	...	...	1,862	1,944	3,806
1916	...	...	...	1,368	1,532	2,900
1917	...	...	...	1,128	1,308	2,436
1918	...	...	...	995	1,032	2,027

Nevertheless, the cost of printing the Journal has been £2,750 8s. 3d., instead of £2,543 7s. 9d. in 1917, so that a reduction of 409 pages corresponds to an increase of £207 0s. 6d. in expenditure; this is owing to further appreciation in the cost of paper and to the necessity of raising the bonus paid to the printers, which now stands at 72½ per cent. on the pre-war rates.

£2,000 National War Bonds were purchased during the year, and the estimated value of the Society's other investments has improved by £414, so that, having regard to the fact that on December 31st, 1918, the cash account was about £420 higher than on the last day of 1917, the assets of the Society show an increase of £2,831, or a total increase of £3,640 if the Research Fund at its present estimated value is included.

The following grants have been made from the Research Fund during the year:

Organic derivatives of bismuth. F. Challenger. ...	£15 0 0
An investigation of the phthalein series. M. Copisarow. ...	10 0 0
The velocity of reaction between the alkyl iodides and sodium methoxide. H. E. Cox. ...	10 0 0
Formation of heterocyclic ring systems by the condensation of chlorocarbamic esters and alcohols. R. L. Datta. ...	10 0 0
The action of alcohols on urea nitrate. P. K. Dutt. ...	5 0 0
Influence of the nitro-group on the mobility of the substituents in the benzene nucleus. J. Kenner. ...	5 0 0
The composition and structure of soaps. J. W. McBain. ...	15 0 0
Melting points of the substituted amides of the normal fatty acids. P. W. Robertson. ...	6 6 0
Synthesis of $\beta$ -phenyl- $\beta$ -hydroxymethylethylamine from cinnamic acid or ethyl cinnamate. E. H. Todd. ...	10 0 0
The space formulae of diphenyl and its derivatives (continued). E. E. Turner. ...	10 0 0
Total ...	<u>£96 6 0</u>

## Liabilities.

To Subscriptions received in advance	£	s.	d.	£	s.	d.
...	...	...	...	284	0	0
...	...	...	...	1	10	0
...	...	...	...	...	...	...
Sundry Creditors, ... ..	...	...	...	...	...	...
" Sundry Debtors, ... ..	...	...	...	...	...	...
Research Fund :—	...	...	...	...	...	...
As per last Balance Sheet	...	...	...	14357	3	4
Add Excess of Income over Expenditure for the year	...	...	...	599	13	9
Chemical Society : Excess of Assets over Liabilities :—	...	...	...	...	...	...
As per last Balance Sheet, ... ..	...	...	...	24758	7	5
Add Excess of Income over Expenditure for the year	...	...	...	2169	4	4
Total	...	...	...	27247	11	9

	£	s.	d.	£	s.	d.
BY Investments (value when acquired):—						
£6730 Metropolitan Consolidated 3½ per cent. Stock	7215	8	6			
£1060 London and North Western Railway 3 per cent. Debenture Stock						
£1520 14s. 3d. Cardiff Corporation 3 per cent. Stock	880	12	0			
£1400 India 2½ per cent. Stock	1650	0				
£2100 Bristol Corporation 2½ per cent. Debenture Stock	1816	1	0			
£2431 Midland Railway 2½ per cent. Preference Stock	2070	2	0			
£1200 Leeds Corporation 3 per cent. Preference Stock	972	2	5			
£1500 Transvaal 3 per cent. Guaranteed Stock, 1929/53	1143	1	0			
£2000 North British Railway 3 per cent. Debenture Stock	1406	13	6			
£700 North British Railway 3 per cent. Debenture Stock	1093	11	0			
£2000 2½ per cent. Stock, 1930/50						
£3100 5 per cent. War Bonds	704	8	6			
£3100 5 per cent. War Bonds	5040	0	2			
(Estimated present value of investments,				29012	0	1
£19,246 14s. 5d.)						
Sundry Debtors	1094	1	1			
Subscriptions in Arrear Estimated to realise...	1650	0				
Insurance paid in advance	460	0	0			
Cash at Bank—Deposit Account	53	2	1			
Current Account	800	0	0			
Cash in hand	953	9	0			
Research Fund:—	16	14	10			
Investments (value when acquired):						
£1200 North British Railway 4 per cent. No. 1	1010	0	0			
£4000 Metropolitan Consolidated 3½ per cent. Stock	4347	18	0			
£1034 Great Western Railway 2½ per cent. Debenture Stock	1040	15	11			
£1142 16s. New South Wales 3 per cent. Stock	1000	0	0			
£1122 Metropolitan Water Board 5 per cent. "B" Stock						
£1305 Midland Railway 2½ per cent. Debenture Stock	1002	16	9			
£1305 Midland Railway 3 per cent. Stock	1010	0	9			
£806 Victoria 3 per cent. Stock	769	6	2			
£498 11s. 6d. 5 per cent. War Stock	4267	4	10			
(Estimated present value of Research Fund Investments, £12,913 19s. 8d.)				14954	2	5
Cash at Bank...				262	14	8
				£43,221	4	2

Q 2

I have examined the above Balance Sheet and accompanying Income and Expenditure Accounts with the Books and Vouchers of the Society, and certify them to be in accordance therewith. I have also verified the Balance at the Bankers and the Investments.

W. B. KEEN,  
Chartered Accountant,  
23, QUEEN VICTORIA STREET, F.C.  
March 5th, 1919.

Approved—C. F. CROSS,  
GEORGE SENTER,  
ARTHUR R. LING.

## INCOME AND EXPENDITURE ACCOUNT

		<i>Income.</i>			
		£	s. d.	£	s. d.
To Life Compositions ... ..	..*			340	0 0
" Admission Fees ... ..				956	0 0
" Annual Subscriptions—					
Received in advance, on account of 1918 ... ..		139	3 4		
" during 1918 ... ..		4729	16 8		
" " " " 1917 ... ..		392	0 0		
" " " " 1916 and previous ... ..		62	0 0		
		5323	0 0		
Less amount included in last year's Income, being valuation of					
Arrears as per last Balance Sheet ... ..		400	0 0		
		4923	0 0		
Add Arrears at date: 1918, £670; 1917 and previous, £524, estimated					
to realise as per Balance Sheet ... ..		460	0 0	5383	0 0
„ Lately Subscribers ... ..				9	0 0
Investments:—					
Dividends on £6730 Metropolitan Consolidated 3½ per cent. Stock ...		170	15 8		
" £1050 London and North Western Railway 3 per cent.					
Debenture Stock ... ..		23	4 7		
" £1520 14s. 3d. Cardiff Corporation 3 per cent. Stock ...		33	1 6		
" £1400 India 2½ per cent. Stock ... ..		25	7 6		
" £2400 Bristol Corporation 2½ per cent. Debenture Stock ...		42	0 0		
" £4341 Midland Railway 2½ per cent. Preference Stock ...		79	7 2		
" £1200 Leeds Corporation 3 per cent. Debenture Stock ...		26	2 0		
" £1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53		31	10 0		
" £1200 North British Railway 3 per cent. Debenture					
Stock ... ..		25	18 1		
" £700 Canada 3½ per cent. Stock 1930/50 ... ..		20	6 0		
" £5200 5 per cent. War Stock and War Bonds ... ..		205	8 3		
„ Income Tax Recovered ... ..		170	0 1		
„ Interest on Deposit Account ... ..		27	7 2	880	8 0
„ Publication Sales:—					
Journals ... ..		1728	6 0		
Proceedings ... ..		2	4 6		
Collective Index ... ..		33	17 2		
Library Catalogue ... ..		1	1 9		
Atomic Weight Tables ... ..		10	6 6		
Annual Reports on Progress of Chemistry ... ..		245	9 6		
Memorial Lectures ... ..		3	1 1		
Jubilee Volumes ... ..		0	17 6		
		2015	8 0		
Less Publishers' Commission ... ..		194	12 11	1820	15 1
„ Proceeds of Advertisements in Journal ... ..		£408	8 0		
Less Commission ... ..		29	8 4	373	19 8
„ Miscellaneous Receipts ... ..				8	6 2
„ Subscriptions from other Societies ... ..				22	1 0
„ Donations to Library ... ..				280	5 0

£10,082 14 11



## FOR THE YEAR ENDED 31ST DECEMBER, 1918.

<i>Expenditure.</i>		£	s.	d.	£	s.	d.
B <sub>3</sub> Expenses on account of Journal :—							
Salary of Editor, including Indexing ... ..		630	0	0			
Salary of Sub-Editor and Assistant ... ..		250	0	0			
Editorial Postages ... ..		31	18	5			
Abstractors' Fees ... ..		240	12	1			
Printing of Journal ... ..		2760	8	3			
Binding ... ..		82	2	6			
Printing of Advertisements ... ..		164	13	2			
Wrappers and Addressing ... ..		4	5	4			
Distribution of Journal ... ..		398	19	4			
Authors' Copies ... ..		111	11	1			
Insurance of Stock ... ..		14	11	8			
					4559	1	10
„ Annual Reports on the Progress of Chemistry ... ..					460	4	9
„ Purchase of back numbers of Journal ... ..					6	4	8
„ List of Fellows ... ..					128	6	2
„ Library Expenses :—							
Salary of Librarian and Assistant ... ..		371	17	0			
Books and Periodicals ... ..		190	1	8			
Binding ... ..		42	4	6			
					613	8	2
„ Indexing for International Catalogue ... ..					30	0	0
„ Donation to International Commission of Publication of Annual Tables of Constants and Numerical Data, Chemical, Physical and Technological ... ..					10	0	0
„ Donation to Board of Scientific Societies ... ..					5	5	0
„ Administrative Expenses :—							
Salary of Staff ... ..		539	15	0			
War Bonus ... ..		254	6	7			
Wages (Commissionaire, Housekeeper, and Charwoman) ... ..		215	19	0			
Coal and Lighting ... ..		61	18	1			
House Expenses and Repairs ... ..		87	2	4			
Furniture ... ..		8	3	0			
Tea Expenses ... ..		35	3	3			
Insurances ... ..		39	6	6			
Accountants' Charges ... ..		21	0	0			
Commission on Recovery of Income Tax ... ..		8	10	0			
Law Costs ... ..		10	10	0			
Miscellaneous Printing ... ..		129	4	6			
Stationery ... ..		129	17	4			
Postages ... ..		105	19	8			
Miscellaneous Expenses ... ..		31	11	2			
					1681	6	5
Balance, being excess of Income over Expenditure carried to Balance Sheet ... ..					2489	4	4



Although one disbursement (£10) only was made in 1917, the balance of income over expenditure for 1918 is £539 13s. 9d., as against £553 2s. 0d. for the previous year. This is explained by an increase of £50 11s. 3d. in the proceeds from investments, of £20 8s. 3d. in repayments of research grants, and of £14 0s. 3d. in the amount of income-tax recovered. £816 19s. 9d. Five Per Cent. War Loan was purchased for this account during 1918.

A vote of thanks to the Auditors proposed by the TREASURER was seconded by Mr. R. G. DURRANT, Dr. G. SENTER making acknowledgment.

On the motion of Mr. W. BARLOW, seconded by Mr. W. F. REID, a vote of thanks was proposed to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year. Acknowledgment was made by Dr. F. L. PYMAN.

The ballot was then declared closed.

The PRESIDENT delivered his Address, entitled "Chemistry in the National Service." A vote of thanks to the President for his services in the Chair and for his Address, coupled with the request that he would allow the Address to be printed in the Transactions, was moved by Professor H. E. ARMSTRONG. Col. C. T. HEYCOCK seconded the motion, which was carried with acclamation, the PRESIDENT making brief acknowledgment.

The report of the Scrutators was presented, and the PRESIDENT announced that the following had been elected as Officers and Council for the ensuing year:

*President.*—Sir James Johnston Dobbie, M.A., D.Sc., F.R.S.

*Vice-Presidents who have filled the Office of President.*—Henry Edward Armstrong, Ph.D., LL.D., F.R.S.; Alexander Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, O.M., D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; Harold Bailly Dixon, C.B.E., M.A., Ph.D., F.R.S.; Percy Faraday Frankland, Ph.D., LL.D., F.R.S.; Augustus George Vernon Harcourt, M.A., D.C.L., F.R.S.; William Odling, M.A., M.B., F.R.S.; William Henry Perkin, Sc.D., LL.D., F.R.S.; Sir William Jackson Pope, K.B.E., M.A., D.Sc., F.R.S.; James Emerson Reynolds, Sc.D., M.D., F.R.S.; Alexander Scott, M.A., D.Sc., F.R.S.; Sir Edward Thorpe, C.B., LL.D., F.R.S.; Sir William Augustus Tilden, D.Sc., LL.D., F.R.S.

*Vice-Presidents.*—Frederick George Donnan, M.A., Ph.D., F.R.S.; Henry John Horstman Fenton, M.A., Sc.D., F.R.S.; Arthur Smithells, C.M.G., F.R.S.; James Walker, D.Sc., LL.D., F.R.S.; William Palmer Wynne, D.Sc., F.R.S.; Sydney Young, D.Sc., F.R.S.

*Treasurer.*—Martin Onslow Forster, D.Sc., Ph.D., F.R.S.

*Secretaries.*—Samuel Smiles, O.B.E., D.Sc., F.R.S.; James Charles Philip, O.B.E., M.A., D.Sc., Ph.D.

*Foreign Secretary.*—Arthur William Crossley, C.M.G., D.Sc., F.R.S.

*Ordinary Members of Council.*—Julian Levett Baker; Alexander Findlay, M.A., D.Sc., Ph.D.; Francis Ernest Francis, D.Sc., Ph.D.; John Addyman Gardner, M.A.; Arthur Harden, D.Sc., Ph.D., F.R.S.; Thomas Anderson Henry, D.Sc.; Charles Alexander Hill, B.Sc.; James Colquhoun Irvine, D.Sc., Ph.D., F.R.S.; Charles Alexander Keane, D.Sc., Ph.D.; Robert Howson Pickard, D.Sc., Ph.D., F.R.S.; Sir Robert Robertson, K.B.E., M.A., D.Sc., F.R.S.; Edward William Voelcker.

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## PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, March 27th, 1919.

By SIR WILLIAM J. POPE, K.B.E., F.R.S.

### *Chemistry in the National Service.*

SINCE the autumn of 1914 a great change has taken place in the public attitude towards the natural sciences, and towards chemistry in particular. One of the recognised duties of the spokesmen of science during the past sixty years or more has been that of endeavouring to bring home to the general public and to its administrators the danger of neglecting the cultivation of pure and applied science. The eloquent discourses of our predecessors, Lyon Playfair, Roscoe, Meldola, and the veterans happily still with us, Tilden and Armstrong, all past-presidents of our society, on the national importance of chemistry, are well known to all of us, but we cannot claim that these utterances produced an effect compatible with their gravity.

Recent events have, however, given a stimulus to the popular appreciation of the need for wider application to scientific investigation of all kinds, which is incomparably greater than had been excited by the previous half-century of the spoken and written word. It may be useful at the present time to consider a few of the causes for this change in public opinion, partly because of the clarification of ideas which emerges from free discussion, partly because of the desirability of recording certain facts and particulars which may be of value to future historians of the strenuous period now ending and giving place to another still more strenuous.

At this time four years ago an urgent call was made for the services in a military capacity of all the chemists who could be spared from civil life. Large numbers were taken into the Army and formed the nucleus of the magnificent Gas Warfare Service, which has been slowly but efficiently developed. Many of these colleagues of ours are now returning to their legitimate spheres in the industrial and scientific life of the Empire, but many will not return; among those who have fallen I would refer more particularly to one who is well known to most of us present for the

invaluable services which he rendered on the defensive side of chemical warfare. Lieut.-Colonel Harrison was one of the great discoveries of the War, and his death on the eve of the armistice was one of its many great tragedies; the protection against gas poisoning which has been employed by our own and allied troops, a protection far more efficient than that ensured by the devices elaborated at leisure by the Central Powers, was due mainly to his wide knowledge, great organising ability, and unfailing resourcefulness in emergency. A movement for the establishment of a memorial to Colonel Harrison was set on foot by the Chemical Warfare Committee, of which he was the Controller at the time of his death, and a considerable sum has been collected from those who had been associated with him in his work for the Services. The Chemical Warfare Committee have approached the Council of the Chemical Society, and have offered under certain conditions to place a memorial tablet or other suitable permanent memorial in these rooms, and also to establish, under certain further conditions, a trust fund to be held by the Society. The Council have with great pleasure intimated their willingness to accept these gifts, and one of the first duties of your new Council will be to decide how best to carry out the provisions of the trust deed.

The efficiency of the British gas protection, which called for the exhibition of so much scientific skill both in research and in manufacture, and led to its adoption by our Allies, is one striking illustration of the paramount importance of science which has appealed to the general public. This subject is, however, but a small branch of the enormous chemical problem which presented itself to the nation nearly five years ago and led to the organisation under Lord Moulton of the Department of Explosives Supplies. During the working out of this problem, issues presented themselves which are probably dissimilar from any that have ever arisen before.

Thus, as the magnitude of the struggle became gradually obvious, it was realised that the whole of the resources of the Empire would have to be utilised fully if success was to be attained. A census of all available chemical products had to be taken, and schemes for their exploitation laid down; all materials had to be apportioned out in accordance with the principle that whatever was used for the manufacture of one particular war material left a corresponding shortage of raw material in connexion with the manufacture of some other, and perhaps equally essential, product. The intricacy of gauging the chlorine output of the country, of determining how to increase it at the maximum rate without unduly disturbing other interests, of apportioning it

most advantageously for use as liquid chlorine and for the manufacture of phosgene, sulphur chloride, carbon tetrachloride, bleaching powder, and many other war materials, is such as would disarm criticism even if the result had been failure instead of brilliant success. This novel mode of presentment, involving recognition of the principle that the Empire could only dispose of certain limited and measurable quantities of raw materials, was but one of many fresh views which forced themselves upon a newly created Ministerial Department. Labour, fuel, and transport had to be discussed in an analogous manner.

The cessation of hostilities found this country manufacturing, roughly, 100,000 tons per annum of nitric acid and sulphur trioxide, with an efficiency of about 93 and 91 per cent. respectively of that theoretically obtainable; we were also making 60,000 tons of T.N.T. and 35,000 tons of cordite per annum. These productions were for all practical purposes on a permanent basis, and could have been continued indefinitely. The factories necessary for securing this huge production were erected by the Government, and for several reasons. First, for economy in production. In spite of the large initial cost of installation, and including rapid amortisation, the national production of cordite was better in quality than, and of approximately one-half the cost of, that imported from America. Secondly, for certainty of supply, which could be ensured only by a home production not subject to the risks of over-sea transport.

With this necessity for gigantic production, the urgency for economy in manufacture necessarily went hand in hand. One of the most interesting documents of the war is the second report on costs and efficiencies for H.M. factories controlled by the Department of Explosives Supplies, which has been recently issued. This report contains a minute analysis of the working costs for each period of each factory engaged on individual items of manufacture; it states what proportion of the cost per ton of product is borne by labour, raw materials, fuel, maintenance, etc., and provides an incitement to further effort towards economy of working by giving a "bogey" cost sheet made up of the most efficient details of cost selected from the complete analysis of expenses. It will be clear that an immense amount of organising power was required to achieve this stupendous result; it was due largely to the genius and energy of Mr. K. B. Quinan.

It must be remembered, however, that this permanent memorial to British chemical activity in production was rendered possible only by the intense effort of the army of chemists and engineers enlisted under the command of Lord Moulton. The necessity for

utilising all the chemical resources of the country to the utmost led, in direct relationship with the census of raw materials previously mentioned, to the attempt to extract the last possible fraction of efficiency in each component process. The huge production just indicated made it very profitable to carry out a vast amount of careful scientific investigation of details of manufacture; so many Fellows of this Society devoted their best efforts to this work that it would be invidious to mention names. Our colleagues have had ample opportunity to realise that the romance of war is now to be found in the laboratory, the workshop, and the factory quite as much as on the battlefield.

An instructive example of the operations of the struggle for economy in the production of a given effect is found in the rivalry which arose between picric acid and ammonium nitrate for use as high explosives. Picric acid costs about £185 per ton to make, ammonium nitrate about £50, and T.N.T. about £100 per ton; the high cost of picric acid means, of course, limited production. A mixture of 80 parts of ammonium nitrate with 20 parts of T.N.T., known as amatol, was introduced early by the Research Department at Woolwich, as being about 5 per cent. more powerful as a high explosive, less "brisant," and more difficult to detonate, and, of course, far less costly to manufacture. The course of the war has been marked by continued progress at the hands of our research chemists in the preparation and applications of amatol; the growing appreciation of the merits of this material led to the discontinuance of the manufacture of picric acid in this country last summer, to the adoption of amatol in place of picric acid as the American standard high explosive, to the approaching elimination of picric acid from the Italian military programme, and to the replacement, in the main, of picric acid by amatol in the French service.

A very pertinent question arises in connexion with the fact that our production of the chemical materials needed for a great European war was negligibly small in 1914 and has gradually attained satisfactory dimensions. We know that the great chemical factories of Central Europe could divert their peace production of chemical products to a war output at very short notice. None of these huge installations requires much time for the design and construction of chemical plant for new purposes; all possess a series of standard items of equipment which can be fitted together rapidly to form a piece of plant capable of use for throwing any ordinary laboratory operation into large-scale practice. Stills, condensers, pressure vessels, filter presses, cooling arrangements of coils and



the like, are available in standard sizes and with standard fittings in such a manner that the installation on a works scale of a laboratory operation is deprived of its most formidable difficulties. The question which demands an answer is why, when the German works were in existence and could attain a war production so quickly, were the Allied nations given time to gradually develop their war production of explosives, noxious materials, etc., from nothing? The question is best answered by an example.

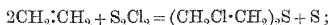
In July, 1917, the Germans first used against the Allies a new offensive material,  $\beta\beta$ -dichloroethyl sulphide,  $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{S}$ , and with very great success. This substance, the so-called "mustard gas," has but little odour, and exposure to it causes comparatively few fatalities; inhalation of, or contact with, its vapour gives rise to acute pneumonia, to the production of painful sores, and to temporary or even permanent blindness. Whilst, as has been stated, the actual mortality is low, and the use of the substance may to this extent be described as humane, the casualties produced are very numerous; slight exposure to a material so toxic and so difficult to detect leads, in general, to six weeks in hospital. The preparation of  $\beta\beta$ -dichloroethyl sulphide was described by Victor Meyer in 1886, and involved the several operations indicated by the following set of equations:

- (1)  $\text{CH}_2\text{:CH}_2 + \text{HClO} = \text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}.$
- (2)  $2\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH} + \text{Na}_2\text{S} = (\text{HO}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{S} + 2\text{NaCl}.$
- (3)  $(\text{HO}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{S} + 2\text{HCl} = (\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{S} + 2\text{H}_2\text{O}.$

When it is realised that operation No. 1 is difficult and that the products of reactions (1) and (2) are soluble in water, it will be understood that no small difficulties must present themselves in the manufacture of  $\beta\beta$ -dichloroethyl sulphide by this process on a large scale. The examination of the German product made it quite clear, however, that the process of manufacture adopted was that indicated by the above set of equations; the over-all yield of product is perhaps 40 to 60 per cent. of the theoretical. In view of the difficulties of manufacture, it was fairly certain that no chemical installation for its production could be established under the control of the Allies within any reasonable time; the Central Nations thus supposed that they held the monopoly of a very powerful instrument of war.

Most British organic chemists were, I think, amazed at the method of production adopted by the German manufacturers; to apply such a technically cumbrous process for the manufacture of so simple a compound seemed quite irrational. By the end of

January, 1918, a process for making  $\beta\beta$ -dichloroethyl sulphide had been worked out in the British laboratories, which consisted of the reaction expressed by the following equation:



the yield obtained in the laboratory was 98 to 99 per cent. of that theoretically possible. The new method was communicated to France and America, and installed by the three Great Allies on a large scale; at the conclusion of the armistice the available daily production of mustard gas by the Allies was equal to the monthly production of the Central Nations.

The answer to the question just put is now available. The German chemical service was inefficient; the scientific chemists under its control were incompetent.

The Allied production of mustard gas had a potentiality of the order of thirty times as great as that of the German; the cost of the German material was of the order of thirty times as great as that of our product. Cost of production under the conditions prevailing for this particular material means, in the end, expenditure in labour; that we were able to produce at something of the order of one-thirtieth of the cost of the German production means that by the allocation of the same quantity of raw materials we could secure thirty times the output. The relative strain on the productive resources of the Allies and the Central Nations caused by a demand for a certain quantity of "mustard gas" is measured roughly by the indicated ratio of one to thirty.

Whilst many instances similar to that of mustard gas might be quoted to show that Germany has been badly served by her scientific men during the war, it would be difficult to overrate the effects of the skill and perseverance exhibited by the German chemical manufacturer. The command of great and long-established factories for fine chemical manufacture enabled the German technologist to throw faulty academic projects rapidly into large-scale production; the cost, namely, the strain on national resources, was enormous, but that an output could have been achieved is a significant tribute to the potentialities represented by the large German fine chemical factories. Both in Britain and Germany production in chemical manufacture has been multiplied during the war, but necessarily in a different manner. Our large production is almost entirely of war importance, and most of the works installed during the war must now be dismantled as a result of the cessation of hostilities; the German expansions, on the other hand, constitute a permanent addition to the potentialities of peace manufacture of staple marketable products. The war has left Germany

with vastly increased resources as a manufacturer of much needed chemical products.

The view that our country is superior to Germany in the possession of creative scientific power has always been maintained in modern times by students of philosophy and history; the correctness of the view has been amply demonstrated during the last four years. Whilst our nation has overcome its initial handicap by a continuous flow of novel scientific devices of military value, our enemies passed through the war with little more in the shape of novel effects than those laboriously elaborated during the preceding years of peace. The more brilliant position which Germany has so long held in applied science arose from the keen appreciation exhibited by German public and official authorities of the rich economic fruits to be reaped from the systematic exploitation of scientific industry as compared with the neglect of scientific effort shown by corresponding classes in this country. Even yet, but small encouragement exists for those who desire to see pure and applied science flourish as it deserves in Great Britain; although it may be long before the scientific industries of Central Europe regain their former predominance, there seems but little prospect of sufficient official encouragement being given in this country to scientific and industrial initiative to ensure our position in the competition with other nations.

In this connexion it is interesting to notice what is happening in the United States. Immediately after her entry into the war America initiated a census of chemists, and in July, 1917, a fully detailed description was available of some 15,000 chemists resident in the States; a research staff consisting of 1200 technical men with appropriate assistance was enlisted for the Research Division of the Chemical Warfare Service alone. Since America was only in the war for about eighteen months this powerful organisation had not time to make its efforts properly felt. Apart from small improvements or changes in detail, practically all the American chemical equipment, both for offence and defence, was manufactured on the detailed plans furnished by Great Britain or France; the available time was too short to allow full play to American genius for novelty and for magnitude of production. The necessity for co-operation brought large numbers of young and active American chemical officers to Europe; it gave those officers for eighteen months the entry to practically every chemical works of importance in England and France, and unrivalled opportunities for accurately judging European chemical methods and markets. These men have now returned to their ordinary scientific and technical pursuits in the States, and it cannot be expected that they have left behind them

the unique experience which they have gained of European conditions.

We may anticipate that competition in pure and applied chemistry between Europe and America will become increasingly keener during the years to come. The competition is already intense, and gives little promise as yet of turning in our favour; it is, in fact, difficult to see how many of the staple products of fine chemical manufacture can hold their own in Great Britain against American competition under the conditions which arose during the first three years of the war. During these years peace production flourished in the States free from Government control, whilst in this country the establishment of a fine chemical industry in war time was naturally rendered far more difficult by State control of works, materials, and labour. The bearing of this may be made clear by an instance. The manufacture of "saccharin" was installed in England after the outbreak of war, but the production was controlled in that the manufacturers were only permitted to sell at a profit of 10 per cent. on the cost, this profit being, in turn, subject to the excess profits tax; further, to prevent the economic difficulties which were foreseen if "saccharin" competed with sugar, the price of English-made "saccharin" was fixed at a figure which involved the very large addition of thirty shillings per pound to the price, this addition being appropriated by the Government. Simultaneously, "saccharin" was manufactured free of all control in the States; it came into this country unrestricted and on such terms that the American producer took the thirty shillings per pound just mentioned in addition to the considerable profit previously made by reason of lower cost of manufacture. America having thus been assisted by our Government to build up a large reserve of profits, is now actually selling "saccharin" in England at eleven shillings per pound—a price at which it cannot be produced here—apparently with the legitimate trade purpose of destroying the English manufacture and subsequently running up the price.

Many cases may be quoted as closely analogous to that of "saccharin," notably in connexion with acetic acid, glycerol, acetone, and methyl alcohol and their products, in which British procedure has facilitated profiteering in foreign countries during the war. The excess profits tax operated insidiously in tempting British manufacturers to keep prices high so as to retain a margin with which to write off capital expenditure in spite of the tax; the foreign competitor, free from Government control of raw materials and exempt from the excess profits tax, was able to take full advantage of the ruling high rates. It will be of interest to see how the problems introduced by these actual occurrences are to be solved advantage-

ously for Great Britain in the great reconstruction upon which our administrators are now engaged.

Sufficient has probably now been said in justification of the rapid appreciation of science, and especially of that branch of science with which we are particularly concerned, in the public and administrative eye. The sudden incidence of new scientific modes of military and naval attack and the quick improvisation and development of equally scientific means of reply, both of which have been so frequently exhibited during the past five years, must have seemed uncanny to the lay observer, who only realised the effects but did not understand the causes.

At the present time, however, most Fellows of this Society have little leisure to reflect on the ghastly tragedy in which it has been our privilege to assist; the curtain has fallen upon this, but is rising again on the greatest epoch in the history of the world. The coming struggle for scientific and industrial position, on the results of which must rest the whole intellectual, artistic, and material future of our race, will call for longer, greater, more persistent and more intelligent effort than any which we have hitherto exerted. We are forced to consider whether we have reason to hope that the recent lessons have been well brought home and whether the free play given to scientific creation and production during the last five years is to persist unhampered in the future. For purposes of war our administrators gave every incentive to scientific investigation; money, men, and material were provided for the asking, free from Treasury control, free, in fact, from all control other than that of the scientific worker able and willing to organise and execute a necessary piece of work.

I see no reason to think that the lesson has been properly learnt and every reason to anticipate a re-establishment of that parsimonious treatment of scientific effort which seems now to belong to a past age, but with which we were all well acquainted five years ago. The control of scientific research is again leaving the hands of the scientific man and being resumed by the lay administrator. The old remark has been resuscitated quite recently that "it is a common-place among administrators to fear the expert." The non-technical administrator has no means of distinguishing the expert from the charlatan; he has perforce to regard the scientific expert as the lineal descendant of the "adept" of alchemical times whose claim to recollection is based upon the adroitness with which he was able to divert public funds to his own base purposes.

It is quite clear that if scientific research is to be assisted by the State—and unless so aided it will languish and carry with it into decadence every activity of the Empire—it must be adminis-

tered by men of scientific training and eminence; any other mode of procedure will necessarily lead to the strangulation of scientific effort by departmental red-tape. In this connexion it is again instructive to refer to American practise; our blood-relatives across the Atlantic had three years in which to study in peace the efforts which we were making in war, and it cannot but be useful to observe the manner in which they propose to profit by our experience.

In 1916, President Wilson, a University professor and an expert, now one of the most imposing figures in terrestrial affairs, called upon the National Academy of Sciences at Washington to nominate the members of a "National Research Council"; the object of this new organisation was stated to be that of co-ordinating the scientific work of the country in order that the scientific problems both of war and of peace might be more efficiently solved. The National Research Council is under the presidency of one of the most eminent among the active American men of science, Professor George E. Hale, of the Mount Wilson Observatory, and has large funds at its command for research purposes. Two points are conspicuous in connexion with the American programme: first, the substitution of the professional lay administrator by the ordinary office staff; secondly, the recognition of the close interdependence of pure and applied science. The contention which has long been advanced in this country, that an adequate output of purely academic chemical research work and the existence of a flourishing, fine chemical industry are mutually essential, is here tacitly accepted; the former seeks in the industries remunerative positions for the products of its training, and the fine chemical industry looks to the scientific investigator for inspiration and new directions for enterprise. The nation which possesses an extensive organic chemical industry controls chemical warfare, the production of pharmaceutical and photographic products, the textile industry, and many other great departments of human activity.

The operations of the great American organisation for the stimulation of scientific research work are already making themselves felt. They have produced just recently an entirely novel method for oxidising naphthalene to phthalic acid, presumably by the use of atmospheric oxygen and a catalyst, which gives a 95 per cent. yield, and are responsible for the huge nitrogen fixation scheme now under installation in the States. These two illustrations alone, the one small and the other large, leave us in no doubt as to the influence which the National Research Council is destined to exert on scientific and technical progress throughout the world.

If British science is to make itself adequately felt in the great

intellectual and material advances of the near future, British men of science must be entrusted with the initiative power and the command of money which they have enjoyed during the past few years; unless this is done our Empire will, as before, continue to fall behind other great nations as a contributor to the increasing mass of pure and applied scientific knowledge.

In an address which I had the honour of delivering in this room a year ago attention was called to the necessity for closer co-operation between the large Societies representing the various chemical interests in Great Britain. During the past year action has been taken in this matter, and some fifteen of the Societies have collaborated in the establishment of a Federal Council for Pure and Applied Chemistry, the functions of which is to advance, safeguard, and voice the interests of chemical science. The Federal Council consists of representatives nominated by the component bodies, and is already occupying itself actively with the questions within its purview; it has moved with some success in connexion with the claims of experimental science to recognition in the recently established scheme for education within the Army, with the provision of fine chemicals for research purposes, with the remuneration of scientific posts, and with other matters. The Federal Council will continue to apply itself to those questions which are of importance to chemists as a class leaving more specific chemical interests to be dealt with by the appropriate constituent societies. A very similar project for the consolidation of the larger chemical interests is in course of execution by our French colleagues.

It is beyond question that a central house for accommodating the chemical societies in a manner more proportionate to their importance than is at present possible should be provided, that a common chemical library far more complete than any now available in this country should be at our service, and that some comprehensive scheme for the publication of compendia of chemical knowledge should be put into operation. A very imposing and costly programme confronts the recent amalgamation of chemical interests, but the universal approval which greeted the proposition for creating a Federal Council for Pure and Applied Chemistry is a happy augury for the future usefulness of the new organisation.

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## OBITUARY NOTICES.

### JOHN PERCY BATEY.

BORN MARCH 22ND, 1889; KILLED IN ACTION APRIL 9TH, 1918.

JOHN PERCY BATEY, M.Sc.(Tech.), was educated at the Manchester Municipal Secondary School, where he was awarded a three years' scholarship to the Manchester School of Technology. He took the degree of B.Sc.(Tech.) in 1908 when nineteen years of age, and was also awarded the Schuster Research Scholarship. Twelve months later he was made M.Sc.(Tech.). For a time he was lecturer and demonstrator, and in 1911 he became assistant to Dr. Liebmann, of Weybridge, where he remained until he enlisted in January, 1915.

He joined the Public Schools Battalion, the Middlesex Regiment, transferring later to the Royal Engineers, and went to France in August, 1915. He was promoted to the rank of Company Sergt.-Major in September, 1916. In 1917 he was awarded the Belgian Croix de Guerre, and in 1918 the D.C.M.

With regard to the D.C.M. the *Gazette* published the following:

"He volunteered on no less than eleven times in one month to conduct parties carrying rations and supplies over a very much exposed area that was being heavily shelled by the enemy to gun emplacements in the front line. The fine example of courage and devotion to duty of this warrant officer had an excellent effect on the N.C.O.'s and men of his company."

F. B.

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### LIEUT. CHARLES WILLIAM DICK.

BORN APRIL 10TH, 1895; DIED ON SERVICE NOVEMBER 9TH, 1918.

LIEUT. CHARLES WILLIAM DICK, R.A.F., died of pneumonia on November 9th last in Cliff Military Hospital, Felixstowe. Mr. Dick, who was the younger son of the late Mr. J. Dick, schoolmaster, North Shields, took 1st Class Honours in his Inter B.Sc.(London) on leaving Rutherford College, Newcastle-on-Tyne, in June, 1912,



and in the autumn of the same year gained an open science scholarship at Cambridge University and became a scholar of Trinity Hall in the autumn of 1913. He passed his final for the B.Sc.(Lond.) in 1914, and on completing two years' residence he postponed further study to become a chemist at Messrs. Curtiss' and Harvey's explosives works at Cliffe, near Chatham, and whilst there was elected a Fellow in 1917. He joined the Meteorological Section of the R.N.V.R. in April, 1918, and after completing his training was appointed meteorological officer at Felixstowe Air Station, and on the creation of the R.A.F. was transferred to its establishment in August, 1918.

J. E. D.

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JAMES HECTOR BARNES, D.Sc.

BORN 1879; DIED 1917.

"I AM sorry to say I have been in very poor health all the summer and had to take six weeks' leave in Kashmir this autumn; it was no holiday, however, for I spent four weeks of it in bed with an irregular pulse—the old story of India, malaria, and, the doctors say, overwork. I hope to come home next summer, for I do not think I can stand another Indian summer here without first having a rest in a decent climate. I shall look you up then, and I hope you will be kind and put me in the way of being useful while at home on leave as I really cannot idle about."

These extracts are from a letter dated November 30th, 1916, received from Hector Barnes. He did not come home, and his prophecy was fulfilled; he did not stand another Indian summer, but at the age of thirty-eight, in the fullness of his intellectual powers, with high hopes and with great opportunities opening before him, he died in India. It is difficult indeed to write any adequate record of the worth and work of such a man. The scientific work which he accomplished, had it been carried out in the most favourable environment, was such as any chemist might be proud to have to his name. But it was carried out under conditions which would only be met by a man of heroic temperament. Such a man Barnes in truth was.

In the plains of Northern India, at Lyallpur, a remote station, on land recently transformed from a sterile desert into a luxuriant agricultural colony by the marvellous system of Indian irrigation, Barnes betook himself in 1906. Born in 1879, he had received his scientific training at the University of Birmingham, where he

studied chemistry and physics under Professors Frankland and Poynting and graduated B.Sc. He had previously been apprenticed to Messrs. Southall and Barclay, pharmaceutical chemists, and the experience of the practical conditions of manufacturing operations which he there acquired no doubt added greatly to his equipment for the work that was in store for him. At Lyallpur he held the position of agricultural chemist to the Punjab Government and professor of chemistry in the Agricultural College, then at the stage of inception. He threw himself wholeheartedly into the work of designing the chemical laboratories, and in 1908 his responsibilities were increased by his appointment as Principal of the College. A year later the College was open for the reception of students. There was an immediate response, as there is to every new educational enterprise in India; but when it was found that the College was not, as it was expected to be, a certain path to Government service, the numbers fell with great rapidity and any belief that there was widespread zeal among neighbouring landowners for agricultural science could not be sustained. Barnes, however, had cherished no illusions, and he knew from the first that the foundation on which he must build was sound scientific research addressed as directly as possible to vital questions of Indian agriculture, and to this he and his colleagues bent their energies. It is not easy to give an idea of what that meant. The physical obstacles imposed by the climate and ever-recurrent sickness, the isolation from the scientific world and from the meagre supplies of apparatus anywhere available in India—these alone might daunt a strong man. Add thereto, only in a more intense form, what we have in England—Government officials in authority whose "humanisation" has precluded the slightest knowledge of what science is, what it does, and how it can be applied to do more—and it may be understood that it is only the very exceptional man who can succeed. This Barnes did in the most conspicuous degree. Standing in the laboratories at Lyallpur after some hours' journey from Lahore through great tracts of solitude and finding apparently all the resources of a European university science department and men busily engaged in employing the experimental methods of modern physical chemistry in the elucidation of fundamental problems in agriculture, the greatness of the achievement was very striking to the imagination. Within a stone's throw were the mud walls of an Indian village with its population living unchanged in the beliefs, the thoughts, the habits of life and work that belong to distant centuries of the past.

The chief lines of work on which Barnes was engaged were salt lands and their reclamation; seepage and the rising of ground water—

level under irrigation conditions; the sugar cane and the sugar industry in the Punjab; the intensity of solar radiation; the Kangra tea industry; the chemical aspect of weevil attacks upon wheat. It is to be feared that his published papers and records will give no adequate idea of the comprehensive plans which he had in his mind in relation to the elucidation of these problems. He talked of them eagerly and in the most interesting way, showing at once his sound knowledge of fundamental science and his appreciation of practical conditions. He had erected a workshop and turned out from it many of the fine tools required in his work, and his laboratory methods exhibited the play of great experimental skill and resource. Space does not admit of any extended account of these investigations, but a little more may be said of one of them. On his last visit to Lyallpur in 1914 the writer was taken by Barnes to Narwala. This spot is twelve miles distant from Lyallpur, and is, or was, infertile salt-land, that is, land which owing to triumph of evaporation over rainfall has become impregnated with a variety of salts, carbonates, chlorides, and sulphates, especially of sodium, calcium, and magnesium, evident as a crust of "white alkali" or "black alkali" upon the soil. This condition of soil has been the subject of much study in America, but Barnes believed that the work had "failed to prove useful and practical for want of a better knowledge of the scientific principles of the causes of sterility. If such causes had been first investigated time and money would have been saved, and in the end the *practical* result would, as it always does, justify the scientist." Accordingly, Barnes set himself to study as closely as possible the physical, chemical, and biological aspects of the problem. Having satisfied himself of the principles involved, he applied himself to the practical problem of redeeming the land at Narwala, and at the time of the visit referred to a tract of infertile land was being mole drilled. Leaving fields where the leisurely ryot was urging his bullock to pull the wooden plough and gently scratch the surface soil, one passed to the Narwala tract where a Yorkshire artisan was found in contest, doubly bitter to him by the futility of his native tongue, with native inaptitude in dealing with a steam-driven mechanical monster from Leeds. The plan was to mole drain the land and then irrigate out so much of the salts as was shown by Barnes's biological methods to be necessary. The results of this trial were extraordinarily successful, and it is scarcely possible to believe that the luxuriant crops (of which photographs afterwards arrived) can have been grown on what was just before the war a stricken desert. Barnes in the end estimated that the system of reclamation would pay between 300 and 400 per cent. on the capital outlay, and its general application would, of course, add

millions to the wealth of India. He was proposing also to apply the system to non-irrigated areas by the use of water pumped from the subsoil.

In 1914 Barnes married Nora, daughter of the late Colonel Francis Thomas Steven, Indian Army.

As soon as the war began he bestirred himself to bring into action all the scientific and material resources that India could supply, but it is impossible at present to quote his important observations on this subject.

Shortly before his death Barnes, not without some reluctance on his part, left Lyallpur to take up at Pusa the post of chief agricultural chemist to the Government of India. What he might have accomplished from there it is idle to conjecture, but the thought of it only deepens the sense of calamity both to India and to Science that surrounds his untimely death.

Barnes was every inch a man and an Englishman. When the writer first saw him he had just come from among his students in the playing fields and was in football attire, a splendid figure of a man, eager, resolute, honest, and kindly. He was beloved by his students and colleagues and respected by everyone. In summing up his qualities in our mind it is impossible not to be struck with the strength and number of endowments that are needed to produce the type of man who is to be the true pioneer of progress in India—endowment of body, mind, and spirit. Happily, such pioneers have been found in the past. They will long be needed in the future of India, and it is difficult to think of any better service to mankind than is open there to those who can bring themselves to the standards that ruled the life and work of Hector Barnes. At Lyallpur his portrait and an annual prize have been set up to preserve his memory, and shortly before his death he was made a Doctor of Science of his University of Birmingham. His work and influence will endure in many fields and many hearts.

A. S.

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### GEORGE CAREY FOSTER.

BORN 1835; DIED FEBRUARY 9TH, 1919.

In the death of Professor Carey Foster in his eighty-fourth year on February 9th, there are many who will feel the loss of a kind and generous friend, to whose gentle sympathy and encouragement much of the happiness, as well as much of the success, of their own lives has been due. A man of extreme modesty and of high

if not commanding ability, Carey Foster had made few direct contributions to scientific literature; but the soundness of his judgment, his almost passionate love of exact knowledge, and his enthusiasm, earned the respect of all, and made his presence invaluable on the many committees of learned societies, the British Association, and the various university boards of which he became a member. An extreme diffidence and a nervous shyness that was not without a peculiar charm to those who came to know him well, as well as a hesitation to express a definite opinion on subjects on which he did not feel on the firmest ground, made it easy to undervalue the services he rendered to science and education during the course of a long and active life.

George Carey Foster was the only son of George Foster, a calico printer and a Justice of the Peace for Lancashire and the West Riding of Yorkshire, and was born at Sabden, in Lancashire, in 1835. After an early education at private schools, he entered as a student at University College, London, where his studies were at first mainly directed to chemistry. He graduated in Honours and with a prize in chemistry in his twentieth year, and acted for some years as chemical assistant to Professor Alexander Williamson, who had then occupied the Chair of Chemistry for six years, and a warm attachment and regard sprang up between the two men. He left England in 1858, and spent some years in study at the foreign Universities of Ghent, where he was a student under Auguste Kekulé, at Paris, and at Heidelberg.

At this time, however, while he continued his chemical studies, his interest became more and more directed to physical science, which was then assuming a position of increasing importance through the work of such men as Clausius, Lord Kelvin, and Clerk Maxwell, and it was natural that the refined accuracy of physical measurements and the readiness which they admitted of mathematical treatment should have presented a strong attraction to a man of his type of mind. The first evidence of his new interest was the appearance in 1863 of two articles on "Heat" in the first edition of Watts's "Dictionary of Chemistry." These articles, extending together to more than 150 pages of closely printed matter, formed an admirably concise and critical statement of the position of an important branch of science, and at once established Carey Foster's reputation as a clear thinker and able exponent of physics.

In the meantime, in 1862, Carey Foster had accepted an invitation to assume the duties of professor of natural philosophy at the Andersonian University, Glasgow, and in 1865 he was encouraged by his friend and former teacher, Williamson, to

become a candidate for the vacant professorship of experimental physics at University College. His election was mainly due to the high reputation he had established as the author of the articles in Watts's Dictionary, and in October, 1865, he entered on his career at the London College, of which he was elected a fellow in 1867, and with which his name will always be associated. He resigned his professorship in 1898, at the age of sixty-three, but was recalled to act as principal of the college for a period of four years from 1900, during a critical time in its history. The last years of his life were spent in the quiet and refinement of a country life on a small estate at Rickmansworth, although, until quite near the end, he was always ready to place his services at the disposal of the educational causes that had been so near his heart in former times. He became a Justice of the Peace for Hertfordshire, and took an interest in politics, in which he was a supporter of the Liberal Party. Towards the end of 1917, after the death of his wife, he began to feel the weight of advancing years, but up to within two weeks of his death he was at work on manuscripts submitted to him for publication in the *Philosophical Magazine*. At the end of January of the present year he had a slight attack of congestion of the lungs, which his heart was not strong enough to resist, and, after gradually becoming weaker, he passed away in the presence of his children on February 9th.

Carey Foster's contributions to chemistry were published between 1857 and 1867. The writer, who is profoundly ignorant in chemical matters, is indebted to his friend, Dr. Forster Morley, for the following summary of these researches. Dr. Morley was engaged in several physical researches under the direction of Carey Foster while a student at University College, and was intimately acquainted with him during the remainder of his life.

"The first paper by Carey Foster appeared in the notes and abstracts appended to the British Association Reports for 1857. It is entitled 'On suggestions towards a more systematic nomenclature for organic bodies.' Gerhardt having introduced the term *homologous* to denote that two carbon compounds differed in their formulæ by  $\text{CH}_2$  or a multiple thereof, Foster now proposed a new adjective, *isologous*, to indicate a difference of  $\text{H}_2$  or a multiple of  $\text{H}_2$ . This adjective is still employed to denote the difference. He further suggested words composed of two Greek numerals, the first of which related to homology and the second to isology. Thus *deutritic* would mean 'belonging to the second homologous series and the third isologous series.' This suggestion, together with many other ingenious proposals for new nomenclature, did not receive support from other writers.

"In 1859 Carey Foster presented a preliminary report to the British Association 'On the Recent Progress and Present State of Organic Chemistry' (*Rep. Brit. Assoc.*, 1859, 1). This was a review of recent work, particularly from the point of view of the development of ideas about formulæ.

"In the Chemical Society's Quarterly Journal (1860, 13, 235) we find a paper 'On Acetoxybenzamic, an Isomer of Hippuric, Acid,' by G. C. Foster. It is dated Ghent, 1860, and is an account of a very careful piece of work carried out under the direction of Professor Kekulé, and describes the first preparation of *m*-acetylaminobenzoic acid, which is shown to be related to hippuric acid, from which it might, in imagination, be derived by an interchange between the radicles of benzoic and acetic acids.

"A paper published in 1861 'On Piperic and Hydropiperic Acids' appeared in the Chemical Society's *Journal* (1862, 15, 17; also in *Rep. Brit. Assoc.*, 1861, 78, and *Annalen*, 1862, 124, 115). In this it is shown that piperic acid,  $C_{12}H_{10}O_4$ , is reduced to hydropiperic acid,  $C_{12}H_{12}O_4$ , and a large number of the salts of the latter are described.

"The most important chemical work carried out by Carey Foster is contained in three papers published in conjunction with Matthiessen. The first is entitled 'Preliminary Notice of Researches into the Chemical Constitution of Narcotine,' and was read before the Royal Society in 1860 (*Proc. Roy. Soc.*, 1861, ii, 55; *Phil. Mag.*, 1861, [iv], 22, 398). In this the authors establish the formula  $C_{22}H_{23}O_7N$  for narcotine, and show that this alkaloid gives off methyl iodide when heated with hydriodic acid. The oxidation of narcotine to opianic acid is discussed, and the formula for opianic acid,  $C_{10}H_{10}O_5$ , correctly determined. It is also shown that, on heating with concentrated potash, opianic acid can be neatly split up into meconin and hemipic acid. A new acid, cotarnic acid, was obtained by the gentle oxidation of cotarnine.

"The second paper on this subject, entitled 'Researches into the Chemical Constitution of Narcotine and of its Products of Decomposition,' was published in 1863 (*Phil. Trans.*, 1863, 345; an abridgment is given in *J. Chem. Soc.*, 1863, 16, 342). The authors here describe how, by acting on hemipic acid with hydriodic acid, an acid,  $C_7H_6O_4$ , which they call 'hypogallic acid,' but which is now known as protocatechuic acid, is obtained. As an intermediate product they isolated 'methylhypogallic acid,' now called 'isovaleric acid.'

"The third paper is entitled 'Researches into the Chemical Constitution of Narcotine and its Products of Decomposition, Part II,' and was read before the Royal Society in 1867 (*Proc. Roy.*

*Soc.*, 16, 39; *J. Chem. Soc.*, 1868, 21, 357). It is shown that opianic acid, when heated with hydrochloric or hydriodic acid, forms methyl chloride or iodide, and a new acid, 'methylnoropianic acid,'  $C_9H_8O_5$ . Thus, opianic acid may be called dimethylnoropianic acid. Methylnoropianic acid yields with nitric acid nitromethylnoropianic acid. Meconin, on heating to  $100^\circ$  with concentrated hydrochloric or hydriodic acid, yields methyl chloride or iodide and methylnormeconic acid, or, rather, methylnormeconin,  $C_9H_8O_4$ . By similar means, narcotine can be converted into methylnornarcotine,  $C_{20}H_{19}O_7N$ .

"These three papers by Foster and Matthiessen made a long step forward in the knowledge of the constitution of the alkaloids, and may, indeed, be termed classical. The accuracy of the work has been amply confirmed by subsequent investigation.

"While this work was in progress, Carey Foster published two papers, entitled 'On Chemical Nomenclature, and chiefly on the Use of the Word *Acid*.' Both appeared in 1865 (*Phil. Mag.*, [iv], 29, 262; 30, 57). In these he protests against the word *acid* being used to denote an oxide, and recommends that  $SO_2$  be called sulphurous oxide,  $SO_3$  sulphuric oxide, and  $C_4H_6O_3$  acetic oxide.

"In 1869 Carey Foster took part in a discussion on the atomic theory, held at the Chemical Society, the subject having been introduced in a lecture by Professor A. W. Williamson. An account of the discussion will be found in the *Chemical Society's Journal* for 1869.

"Carey Foster's work in chemistry shows that if he had decided to devote himself to that science he would have taken a distinguished position among his colleagues. He was a member of the Council of the Chemical Society from 1865 to 1868, again from 1872 to 1875, and again from 1885 to 1886, and Vice-President from 1888 to 1890. His Fellowship of the Society dates from 1856."

During the early years at University College, Carey Foster made a number of contributions of minor interest to scientific journals, but his first important paper, "On a Modified Form of Wheatstone's Bridge, and Methods of measuring Small Resistances," was read before a meeting of the Society of Telegraph Engineers in 1872 (*Telegraph Engineers' Journal*, 1872—1873, 1, 196). Previous to this date, Wheatstone's bridge had provided electricians with a convenient and fairly accurate method for comparing resistances, and, as is well known, the result of the experiment expresses the ratio of one resistance to the other. Carey Foster,



however, so modified the bridge method that the difference between instead of the ratio of the resistances was determined. The advantage of the change is only apparent where the resistances to be compared are of "nearly equal value, as is generally the case, for instance, in the testing of standard coils; but where this condition is fulfilled, the new method transformed the bridge method from being merely a fairly accurate means of measurement into one of the most refined accuracy, comparable with that attained in the use of a sensitive balance. It also supplied the means of dealing with a very small resistance, such as that of a short, thick wire, by determining the difference between it and the zero resistance of a short copper bar, and it was, indeed, for this alone that the method was first suggested. Carey Foster's method has proved of the highest value to the science of exact electrical measurement, and has made it possible to issue standards of electrical resistance of an accuracy that would otherwise have been impossible of attainment. Alike in its simplicity and its refined accuracy, the method is thoroughly characteristic of his mind. He further showed how the principle involved might be applied to the important process of calibrating the wire of the bridge.

In 1881 Carey Foster published "An Account of Preliminary Experiments for the Determination of the Electromagnetic Unit of Resistance, in Absolute Measure" (*Rep. Brit. Assoc.*, 1881, 426). The accurate determination of this important unit had been undertaken by the British Association in 1863, and the value that had been accepted in this country, as well as widely in other parts of the world, was expressed in the "B.A. unit of resistance," the value of which had been determined by a Committee of the Association consisting of Clerk Maxwell, Fleeming Jenkin, and Balfour Stewart. The classical method of experiment adopted by the Committee consisted in revolving a large, flat, closed coil of insulated copper wire about a vertical diameter in the earth's magnetic field and measuring the consequent deflexion of a magnet suspended at its centre. The deflexion was due to the induced current developed in the coil, and this depended on its resistance as well as on the intensity of the earth's magnetic field. The last, however, affecting the induced current and the deflexion equally, although in opposite senses, disappeared in the final equation that expressed the result of the experiment, leaving a relation between the resistance of the coil, its geometrical form and dimensions, and the speed of its revolution.

During the years that had elapsed since the issue of the B.A. unit, the results of other measurements had led to a growing conviction that it was appreciably too small, and Carey Foster

described an experiment in which, whilst the general principle of the British Association experiment was maintained, it was modified in an important detail. The two ends of the wire composing the coil were unconnected throughout the greater part of its revolution; but for a short interval, the centre of which coincided with the transit of the plane of the coil through the magnetic meridian, they were placed in connexion through sliding contacts with the two ends of a standard resistance coil that formed part of an "auxiliary" circuit in which a steady current was maintained by a thermopile. By the principle, originally applied by Poggen-dorff in the potentiometer, no current is developed in the coil if the electromotive force developed in it by its rotation in the earth's magnetic field is equal to the fall of potential between the two points in the auxiliary circuit with which it is connected, this being the product of the current supplied by the thermopile and the resistance of the standard coil, and the method of experiment consisted in so regulating the current of the thermopile that the deflexion of a sensitive galvanometer included between the revolving coil and one of its points of connexion with the auxiliary circuit should disappear, whilst at the same time the deflexion of the magnet of a tangent galvanometer included in the auxiliary circuit was recorded. The general principle is simple, and a relation is readily established between the resistance of the standard coil, the deflexion of the magnet of the tangent galvanometer, the geometrical form and dimensions of the revolving coil, and its speed of revolution.

The chief refinement that Carey Foster hoped to effect in this modification of the original experiment consisted in the possibility of the *direct* determination of the resistance of the standard coil. In the original experiment, the resistance determined was that of the revolving coil, and the resistance of the standard could only be obtained by subsequent comparison. To obtain the maximum induced current, it was essential that the revolving coil should be wound with copper wire, and as the resistance of copper with that of all pure metals is seriously affected by changes of temperature, it was necessary that the temperature of the coil should be known with great accuracy during the time that the experiment was in progress, a very delicate matter. In Carey Foster's method, however, the resistance of the standard coil was directly determined while it formed a part of a fixed and independent circuit. The wire composing it might equally well be of copper or of one of the many alloys the resistances of which are scarcely affected by changes of temperature, whilst it was an easy matter to determine its temperature with great accuracy. Further, the new method

reduced the correction for the self-induction of the revolving coil, an important and rather delicate detail in the original experiment, to insignificant proportions, but, at the same time, it unfortunately introduced the necessity of taking its capacity into consideration, a feature that Carey Foster did not probably at first realise.

The apparatus for carrying out the experiment was constructed with great refinement, and was erected at University College, and a series of preliminary experiments were made by Carey Foster with the assistance of Mr. G. W. von Tunzelmann. These experiments showed that the method was capable of yielding consistent results, and there is no doubt that a far higher consistency would be possible if they were repeated in a modern laboratory more completely removed from the disturbing magnetic influences of large masses of iron of continually varying temperature. The results were not, however, sufficiently consistent to satisfy the critical judgment of Carey Foster, and the experiment was abandoned. Whilst they were in progress, Lord Rayleigh and Professor Schuster were engaged in repeating the original experiment, adopting precautions that experience of the intervening years had been shown to be necessary, and in 1882 they published an account of their experiments, and during the next ten years independent evidence supplied by other methods has shown the value they obtained to be a close approximation to the truth.

In 1886 Carey Foster contributed a paper to the Physical Society of London "On a Method of determining Coefficients of Mutual Induction" (*Phil. Mag.*, 1887, [v], **23**, 121—129), the method depending on the comparison between the coefficient of mutual induction of two coils and the capacity of a condenser. On forming or breaking a current in one of two coils, the primary, a discharge of electricity takes place through a neighbouring, secondary, coil, the discharge being determined by the coefficient of mutual induction of the two coils; also, if the coatings of a condenser are connected to two points of the primary circuit, a charge, proportional to the resistance of that part of the circuit that is included between the two points of connexion, enters the condenser, and will be discharged on the cessation of the primary current. To combine these two examples of "ballistic" discharge, Carey Foster succeeded in so connecting the two circuits that, on the break of the primary current, the condenser was discharged through the secondary circuit in the opposite direction to that of the induced discharge, and on varying the charge of the condenser by regulating the resistance between the points of its connexion with the primary circuit, its discharge and that of the induced current neutralised one another.

The disappearance of discharge in the secondary was indicated by a galvanometer, and a simple relation was given between the coefficient of mutual induction of the coils and the capacity of the condenser. The capability of the method had been thoroughly tested at University College by Mr. F. Womack, and it had been shown to be capable of yielding results of a high order of accuracy. Carey Foster's method of determining the coefficient of mutual induction between two circuits has taken its place among the accurate methods of electrical measurement.

In 1876 Carey Foster devised a method, based on the principle of Wheatstone's bridge, of tracing the equipotential curves in a sheet of tinfoil conveying an electric current, and in collaboration with Sir Oliver Lodge he published two papers, "On the Flow of Electricity in a Plane Conducting Surface" (*Proc. Phys. Soc. London*, 1876, 1, 113, 193), in which this method of experiment was adopted. A further paper by Carey Foster and the present writer, "On the Difference of Potential required to give Sparks in Air," was presented to the Physical Society in 1884 (*Chem. News*, 1884, 114). In the method of experiment adopted in this research, potential differences were measured by a modified form of absolute electrometer that had been designed by Carey Foster and that was found to supply an accurate method for measuring potential differences necessary to produce sparks of from 0.1 to 5 cm. in length.

Among Carey Foster's other publications were further articles on "Heat," "Thermodynamics," "Electricity," and "Magnetism" in later editions of Watts's "Dictionary of Chemistry," and in these he fully maintained his reputation for accuracy, clear judgment, and power of scientific exposition. In later years he published a text-book on electricity in collaboration with Professor A. W. Porter.

Carey Foster became a member of the British Association in 1857, and continued to take an active part in its proceedings until late in life. Besides his direct contributions, to which reference has already been made, he was a member of a number of its committees, the more important of which were those on "Standards of Electrical Resistance," "The Selection and Nomenclature of Dynamical and Electrical Units," "The State of Knowledge of Spectrum Analysis," and "Electrolysis." As President of the Mathematical and Physical Section in 1877, he gave an address on "The Mutual Relation between Mathematics and Physics," in which he dwelt on his favourite theme of the importance of accurate measurement as the foundation of discovery in science. He was Treasurer to the Association from 1888 to 1904. He was one of

the founders of the Physical Society of London, the first meeting of which was held in 1873, and of which he was President for two years from 1887. He acted as President of the Society of Telegraph Engineers, now the Institute of Electrical Engineers, in 1880 and in 1881. He was elected to the Fellowship of the Royal Society in 1859, acting as one of its Vice-Presidents from 1891 to 1893, as well as from 1901 to 1903, and he took a keen interest in the work of Kew Observatory Committee of the Society. He received the honorary degrees of LL.D. from Glasgow and D.Sc. from Manchester.

From the first, Carey Foster took a deep interest in the reconstitution of the University of London. Whilst fully recognising its services to education in its earlier days, he was sensible of the grievous anachronism by which the University of the greatest city of the world should continue to be solely engaged in examining and in conferring degrees. He had a high ideal of a university as a body of men and women earnestly engaged in the pursuit and extension of knowledge rather than in preparation for examinations, and he strove without ceasing to bring about the foundation of a university in London that should be worthy of it. He was an active member of the many early committees the aims of which were a constructive policy that should achieve his ideal, and he felt keen disappointment when the conflicting of many interests made it impossible of full attainment in the present university, although it received his full and loyal support. He never ceased, however, to look forward to a time when, by further reconstruction, London should possess a university fully worthy of its position, and he welcomed Lord Haldane's Report as indicating the possibility of a further step in this direction, and possibly its full attainment.

The writer is indebted to Sir T. Gregory Foster, Provost of University College, for a sketch of Carey Foster's work while acting as Principal of the College from 1900 to 1904.

"Dr. G. Carey Foster resigned the Quain Chair of Physics in 1898. It was a time of crisis in university affairs in London, as the reconstitution of the University was pending.

"In view of the impending reconstitution, the Council of University College appointed a special committee to consider the position of the College. On the recommendation of this committee, the office of Principal, later changed to Provost, of the College was instituted. Dr. Carey Foster was invited to be the first occupant of this office. He held it from 1900 to 1904.

"In his capacity of Principal, he was appointed to represent University College on the Senate of the University under its new

constitution. He threw himself heartily into the new problems that arose, and brought to them all his ripe judgment and experience.

"It soon became evident that the new constitution, under which the University was given a teaching side as well as an examining side, made it desirable that University College, which had been originally founded to be the University of London, should be merged into the reconstituted University. Dr. Carey Foster took an active share in the negotiations that led up to the incorporation of the College in the University. He regarded it as 'a step towards securing unity of aim and interest in all that relates to advanced education and the promotion of original research in London.' He hoped that it was the beginning of a movement that would lead to the concentration and the consolidation of university work in London.

"This view is expressed in the final paragraph of his sketch of the History of University College, which is as follows:

"The step taken by University College has been followed by King's College, which was incorporated in the University on September 1st, 1909. It may be hoped that similar action will be taken by other analogous bodies, and that in course of time the University of London, perhaps with some modification of its present constitution, may become a centre about which the various bodies in London that are qualified to take part in university work may be united into a single organised system, in which they shall supplement instead of competing with each other, each doing the work for which, by its special circumstances, it may be best fitted.'

"During the four years of his Principalship, great progress was made in various directions in the reorganisation and development of university work in London. The plans for the removal of University College School were matured. The buildings formerly occupied by the School were, as a consequence, set free for university purposes. The accommodation provided at University College for university work was materially increased. There was a rapid growth in the intellectual and social activities of the College, and in these Dr. and Mrs. Carey Foster took a prominent share."

At an early period of his work at University College, Carey Foster recognised the importance of practical work in physics as an essential element in scientific education. The first physical laboratory for students had been opened by Magnus at Heidelberg in 1846, and it was followed in 1863 by the addition of a physical laboratory to the University of Berlin. From 1845, Lord Kelvin

had invited his senior students to work in his laboratory, for a time a disused wine cellar, at Glasgow, and his example was followed by Carey Foster, who thus introduced the teaching of practical physics in this country. At the beginning, this work formed no recognised part of the College curriculum, but regular practical courses in physics were arranged in 1867, the laboratories at that time consisting of two of the College rooms, only one of which was fitted with benches. Later, a third room in the basement, known as the "dungeon"—it was indeed a veritable dungeon—was added, and the privilege of working in it was reserved for the professor and students engaged in research. For some years, the only apparatus available was of the simplest character, but instruments were being constantly designed by Carey Foster himself, whilst the designs were executed by a clever Scotch mechanic, William Grant, who acted as his assistant during the whole time of his professorship, and without whom no reference to the laboratory would be complete. Grant, who was quite a character in his own dour way, became a permanent feature of the Physical Department. His love of the apparatus, so much of which he had constructed, and the agony he experienced in seeing it misused, made him a source of terror to all students other than those few who proved themselves worthy to be entrusted with it; whilst many will remember with humiliation his lofty refusal of the tip that was occasionally offered, either from gratitude or from a desire to acquire merit. He was of the most faithful of servants, and was devoted to Carey Foster, whilst each regarded the other with a simple affection of which both alike were worthy. Sir Oliver Lodge, who was a student in the laboratory in those days, and who later became Assistant Professor of Physics at the College, has rendered a grateful as well as a graceful tribute to the educational value of the work done in the old physical laboratory of University College (Letter to *Nature*, December 3rd, 1908).

In the years that followed, physical laboratories for students were opened at other colleges, and it was inevitable that, as many of these were attached to new institutions in which it had been possible to design the buildings with a view to their subsequent use as laboratories, the simple equipment at University College should have been left behind. Carey Foster, in consequence, continually urged the governing body of the College to undertake the building of a physical laboratory that should be worthy of its traditions, although, no doubt by reason of financial considerations, his representations were for a long time without success. At length, however, he had the satisfaction of preparing the plans for the present laboratories, which were opened to students in

1893, and form a fitting memorial to the value of his work as Professor of Physics. There was an old asphalted tennis court within the College walls from which some of us have often returned in exhilaration, although with begrimed hands and flannels, and now only lives in memory; the building that now occupies its former site is the "Carey Foster" Laboratory.

His nervous manner prevented Carey Foster from ever becoming a good lecturer, and his failure in this respect was perhaps due, in addition, to a conscientiousness that made it difficult for him to be content with a simple statement that he knew to be only an approximate expression of a truth, and at the same time made him reluctant to adopt the customary method of illustrating physical laws by the use of simple, although entirely imaginary, experimental data. In place of these, his illustrations would often consist of the actual results of laboratory measurements, and the younger students, unless they were of a rather exceptional type, were apt to lose both attention and interest in the details of laborious computation. The more able students, however, were inspired by this very quality in their teacher. They grew to reverence exact expression and to regard it as the foundation of all scientific knowledge. They continually brought their difficulties to the Professor, and were encouraged to do so by his unlimited patience in dealing with them. It was not unusual to find Carey Foster surrounded by a small group of students engaged in close discussion half an hour after the close of a lecture, although the dining-room had long since claimed the attention of the rest of the College.

The same quality of enthusiasm for his work and his infinite patience in dealing with its smallest details appeared in his work in the students' laboratory. He never found lecturing easy, but after having given a lecture in the morning and having a further lecture for senior students in prospect at the close of a long afternoon, he would frequently come to the help of some duffer in difficulties in the laboratory, and would devote the best part of an hour to the details of a simple experiment in physical measurement. On these occasions, indeed, there was a danger of his being led by his own love of accurate detail, not only to conduct the whole experiment himself, making all the observations, but to carry out whatever computation might be involved, while the student looked on wonderingly, as from a distance. It may be that some who have worked in the old laboratory at University College in those days have preserved the scraps of paper covered with logarithmic calculations that Carey Foster often left on the



benches, all executed in his wonderfully neat writing, as a memento of the most patient of teachers and most lovable of men, but such prescience is rarely bestowed on youth.

His nervousness made conversation with Carey Foster difficult, even to those who came to know him intimately. Whilst, however, it remained a source of some embarrassment to them, his friends came to regard it as so essentially a part of him that it too became lovable, and they would have felt still more embarrassed if he had suddenly succeeded in overcoming it. Closely associated with his manner was a quaint and entirely original sense of pure humour, that found frequent opportunity for expression both in his professional work and in his private life. That his nervousness and hesitation did not arise from any defect in character would be shown, were any such evidence necessary, from his letters. In these, Carey Foster found no difficulty in expressing himself with perfect clearness and precision, whilst both were emphasised by the beauty and strength of his handwriting. It was in his letters, perhaps, that his quaint humour found its best opportunity for expression. Through the kindness of Mrs. Minchin, the writer has before him a number of letters written by Carey Foster to her husband, the late Professor G. M. Minchin, which are so characteristic that little apology is necessary for the introduction of a few short extracts. A close friendship existed between Carey Foster and Minchin, and in their unassuming simplicity and gentleness there was much resemblance between the characters of the two men. Carey Foster had a profound respect for Minchin's mathematical powers, and consulted him when he felt a doubt as to his own grasp of the mathematical treatment of a physical problem, whilst Minchin had an equally deep regard for Carey Foster as an authority on physical matters, and has expressed his regret to the writer that Foster's nervous manner, together with his extreme modesty, should have made it difficult for some, even of his friends, to realise his true greatness.

The first extract is from a letter dated 1882:

"My dear Minchin,

"The lesson of the day touching electric endosmose is written in the First Book of Wiedemann, beginning at the 392nd verse of the second chapter . . . wherein it is written how the ions do wander when a current passeth through their midst. This, I take it, is the whole secret of electric endosmose; the porous diaphragm causeth not the flow, but maketh the same manifest by hindering the return thereof."

The second is also dated 1882:

"My dear Minchin,

"I hope the enclosed may serve your riverence's purpose. Sure, and it's bad I did not write before. But I had to think, and that goes slow.

\* \* \* \* \*

"As to your telegraphic friend; let him take to himself a tangent galvanometer and a set of resistance coils, and sundry cells according to Daniell and Grove. . . ."

and then follow instructions as to what the telegraphic friend should achieve.

An extract from a letter referring to a fairly well-known man:

"The gentleman's surface integral suggests to me a considerable amount of self-esteem. But I am willing to believe that the charge is purely superficial. . . . I am told by a friend who knows him much better than I do that he is a good fellow."

And the last is from a letter written in 1887 congratulating Minchin on his marriage:

"My dear G. M. M.,

"I heard awhile ago that you had entered into combination and were no longer a dissociated atom. Accept my warmest congratulations and my fervent hope that you may appreciate the blessings of home rule more fully from year to year."

Several of the letters deal with Minchin's work with photo-electric cells.

The private life of Carey Foster was one of quiet beauty. His transparent honesty and high regard for truth earned him the respect of his friends, whilst his unvarying kindness and courtesy won their affection. In 1868 he married Mary Anne Frances, daughter of Andrew Muir, of Greenock. Recalling that time, Dr. Forster Morley writes:

"It seems only yesterday when my father (the late Professor Henry Morley) said to me, 'I have been walking round the Square with Carey Foster, who has just told me that he is engaged to be married, and has been speaking most charmingly on the subject of love of a man for a woman.'"

There was a striking resemblance between the character of Mrs. Foster and that of her husband, and she even acquired a suspicion of the nervousness that was so strongly marked in him, that, however, only accentuated a natural charm of manner in her. There were born to them four sons and four daughters, all of whom are still living. The mutual confidence that existed between Carey Foster and his wife, and the evident affection with which both parents were regarded by their children, gave a peculiar charm to the visits of the many friends who were always welcome to their home. Mrs. Foster died in 1917, and a year and a-half later Carey Foster's body was laid to its last rest beside hers in the peaceful cemetery at Rickmansworth.

Among the number of Carey Foster's old students at University College who have become distinguished were Prof. W. E. Ayrton, Sir Oliver Lodge, Dr. H. Forster Morley, Prof. Viramu Jones, Prof. A. P. Chattock, Prof. J. A. Fleming, Prof. T. Hudson Beare, Prof. A. W. Porter, Prof. F. Womack, Prof. J. Sakurai, Sir Victor Horsley, and Prof. W. D. Halliburton. It is from his having been first a student, then a demonstrator, and thereafter a friend of Carey Foster that the writer has been able to pay in this notice his last tribute to the memory of one he loved and admired.

A. H. FISON.

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### WILLIAM JOEL KEMP.

BORN 1841; DIED MARCH 22ND, 1918.

WILLIAM JOEL KEMP was born at Bow in 1841. He was the youngest of three sons, and was educated at Stock's Academy at Poplar. Owing to his father's death, he left school at a very early age, and was placed in the office of a ship's broker. Finding this work very uncongenial, he induced his relatives to article him to Carters and Green, builders of the famous China tea clippers, in the yard which subsequently became the headquarters of the Thames Ironworks and Shipbuilding Company. His apprenticeship commenced at an unfortunate time, for wood was rapidly being replaced by iron in the construction of ships, and the old-established firms which did not move with the times were being left behind. All the same, this period of his life must have been a particularly happy one. He met all sorts of seafaring men, and in later life he never tired of relating anecdotes connected with their superstitions and adventures, and it is not unlikely that their experiences quickened

the sense of imagination which served him so well in after years. Shortly after completing his articles he married Mary, the daughter of John Cayzer, who organised the emigration to Australia of the East Anglian farm labourers in the starving 'forties and 'fifties. About this time he entered the service of Rickett Smith and Company, coal and coke shippers, as buyer. In this capacity he was brought in contact with the lime burning, plaster, and kindred industries, and when in 1876 a company was formed to work the bed of gypsum discovered four years earlier through the Sub-Wealden boring at Netherfield, Sussex, he took a small financial interest in the undertaking. It was about this time that the necessity for technical education and scientific training was first accepted in England. In 1879 the City and Guilds of London Institute for the Advancement of Technical Education was formed, and almost immediately courses in chemistry under Armstrong in temporary premises in Cowper Street, Finsbury, were advertised. Although nearly forty years of age, Kemp, knowing that the manufacture of plaster at Netherfield rested entirely on rule-of-thumb methods, determined to take advantage of the facilities which the City Guilds Institute afforded and to become an efficient chemist. At Cowper Street he worked for one or two days a week, encouraged and inspired by Armstrong, and he soon proved himself to be not only a logical thinker, but an expert manipulator. The other students in the laboratory were all boys, and the writer, who worked at the bench adjoining Kemp's, shared with them the admiration of his power of application and of his rapidly acquired skill. Kemp, influenced by Armstrong's spirit of research, soon began to make investigations on the production of sulphur from gypsum and from alkali waste, and these occupied him for several years. He was the first to suggest making alkali waste into a paste with water and pumping carbon dioxide into the sludge contained in an inverted conical vessel, thus making the gas do its own stirring and bringing every particle of the waste in contact with it. Some of the results of these investigations were subsequently embodied in Rawes's patents, which were worked by Chance. During these years, the position of the Sub-Wealden Gypsum Company at Netherfield had become very critical, the output had fallen below 40 tons a month, the quality of the plaster was bad, and creditors were clamouring for payment of their accounts, which there were no funds to meet. There was already on the bank an immense tonnage of dump, a grey stone considered useless, which had to be hauled to the surface with the white gypsum, and it was becoming increasingly difficult and expensive to dispose of it on the surface. A meeting was held with the object of winding up the company,

but Kemp, who had already begun to experiment with the grey stone, which consisted almost entirely of gypsum, persisted in the view that under proper direction the operations of the company would be successful. Two of the shareholders present were impressed, and agreed to provide further funds if Kemp would undertake the management, and it was thereupon decided that operations should be continued. Kemp's experiments with the grey stone were now pushed on, with the result that in a short time he had perfected a method whereby the waste was converted into a plaster of the Keen's cement variety, which, although dark in colour, set hard and evenly. He introduced this plaster under the name of "Sirapite," and from that day the success of the undertaking was assured. In 1891, 10 tons of "Sirapite" were sold; ten years later the annual sale was 15,108 tons, and in 1911 the sales exceeded 31,000 tons. Kemp's genius was shown not only in the way he attacked his problems on the chemical side, but also in his engineering ability and in the handling of men. From the first he recognised the inefficiency of boilers fed with water almost saturated with calcium sulphate, and within two years of taking control he had scrapped the steam plant and had substituted gas producers and large gas engines. He introduced kilns of large size, which reduced the consumption of fuel and greatly simplified the grinding and mixing plant. He subsequently opened up a new shaft in the mine, which he equipped with electric lighting and haulage plant. Having placed the business on a profit-earning basis, Kemp devoted his attention to the amelioration of the condition of his workpeople. Although himself prepared to work twelve hours a day or more, he reduced in 1895 the working hours to eight and afforded all workmen suitable opportunities for recreation. At his suggestion, the company built a large number of model houses standing in large gardens, which the workpeople were permitted to purchase at cost price. In 1903 Kemp completed his plans by bringing about an amalgamation of the chief makers of plaster in the United Kingdom.

Very few of those who travel by the South-Eastern Railway from Tunbridge Wells to Hastings realise that near Mountfield, hidden from, but within a few hundred yards of, the line, and in one of the most beautiful of the Sussex valleys, lie a mine fully equipped and busy works employing several hundred hands, at which a large part of the plaster used in this country is produced. It was here that Kemp conducted his experiments which revolutionised the industry, and it was here, at the scene of his life's work, that he breathed his last. Shortly after the outbreak of war his son, who for some years had assumed the management, volunteered for

service, and Kemp, then seventy-five years of age, returned to take charge. Always confident and cheerful, ever hard-working, he resumed his former duties with an activity and interest which might have been expected from a man thirty years his junior. On the morning of March 22nd, 1918, he rose in the usual health and spirits, but shortly afterwards, when about to go the round of the works, he suddenly expired.

GERALD T. MOODY.

### SYDNEY LUPTON.

BORN JANUARY 3RD, 1850; DIED JULY 10TH, 1918.

SYDNEY LUPTON, who was elected into the Society in 1872 and remained a Fellow until his death, was the youngest and last surviving son of Darnton Lupton and of his second wife, Anna Jane Busk. He was born at Eller Close, Roundhay, near Leeds, on January 3rd, 1850. His father, a member of a well-known Yorkshire family, was head of the firm of William Lupton and Co., woollen manufacturers. He was a man of considerable influence and public spirit, much respected, and took a leading part in the municipal politics and social life of the town and district.

His son, the subject of this notice, was educated at Rugby and lived in Dr. Jex Blake's house. From Rugby he passed to Oxford, where at Christ Church he came under the influence of Dr. Vernon Harcourt, and was led to devote himself to science, particularly to mathematics and chemistry.

On leaving the University, after taking his degree, he was appointed a science master at Harrow School. The work of school teaching was not uncongenial to him, and he had a fair measure of success in it; but his mother—now a widow—having fallen into indifferent health, he resigned his position in order to live with her at Harehills, near Leeds, where he established a small laboratory and continued to occupy himself with experimental work.

It was during this period that the writer of this notice made his acquaintance, and had the opportunity of observing the progress of his inquiry on the slow oxidation of potassium, the longest and perhaps the most important of his investigations. On the death of Mrs. Lupton he took a smaller house at Roundhay, where he continued to live until his removal to London in 1896.

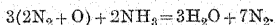
During his residence in Leeds, Lupton took part in the civic life of the town, was a member of the Board of Guardians, and

was associated with the late Canon Jackson, Vicar of St. James's, in many charitable objects. For four years he was a member of the Committee of Management of the Cookridge Convalescent Hospital, and on his resignation, consequent on his leaving Leeds, his fellow-members recorded their appreciation of his genial and energetic help and their sincere thanks for his services "during a period requiring special administration." This last sentence has reference to the assistance he was able to render the institution in connexion with the erection of a wing to the building to perpetuate the memory of his friend, Canon Jackson.

Lupton's intellectual tastes led him to take an interest in the activities of the Leeds Philosophical and Literary Society, where he occasionally lectured on scientific subjects. He became a member of its Council in 1885-6, Honorary Secretary from 1886-95, and a Vice-President in 1895-6.

Practically the whole of Lupton's experimental work was done during his residence at Leeds. His first published paper, "On the Formula of the Alums," appears in the *Journal* of the Society for 1875. Although the doctrine of valency, which we owe to Frankland, was fairly well established at this period, there was considerable uncertainty as to the true formulæ of a number of inorganic compounds, owing to doubt as to the valency of particular elements. This was the case with the group of the alums. Lupton, at the suggestion of Dr. Vernon Harcourt, sought to establish the generic formulæ of these salts, independently of considerations of the combining values of their constituents, by a study of the conditions under which they lose their water on heating or on exposure to a dehydrating agent under reduced pressure, and he showed conclusively that they must contain at least twenty-four molecules of water, whence the general formula now universally accepted follows.

In the same year he published a note on the preparation of cuprous chloride, in which he described the different mode in which water acts on this substance, depending on its method of formation (*Chem. News*, 1875, **30**, 233). This was followed in 1876 by a number of short notices (*Chem. News*, 1876, **33**, 90). He showed that in preparing nitrogen by the well-known method of passing air over red-hot copper turnings, the operation might be rendered continuous by mixing the air with ammonia gas, whereby the cupric oxide was reduced as fast as it was formed, or, as is more probable, by the metal acting catalytically and inducing the production of water:



In this manner, only a relatively short length of heated copper turnings is needed, and the action proceeds uninterruptedly.

In another communication, on the "Solubility of Naphthalene in Water," he sought to disprove Garden's contention that Plateau's theory of the cause of the movement of this substance on the surface of water was invalid by showing that its solubility, and consequent high tension of its solution, are sufficient to account for the phenomenon.

He further described a number of reactions serving to distinguish aniline from naphthylamine, and made known a number of characteristic tests for succinic acid.

Lupton's most important chemical paper was his study of the "Slow Oxidation of Potassium," communicated to the Society in 1876 and published in the *Journal* for that year, in which he carefully repeated the observations of Davy, Berzelius, Gay Lussac and Thénard, and Harcourt, and sought to clear up certain discrepant statements with regard to the number of potassium oxides capable of existence. He confirmed Vernon Harcourt's work, made fourteen years previously (*Quart. Journ. Chem. Soc.*, 1862, **14**, 267), carefully watching the colour changes which follow the progress of the oxidation, and analysing the products at the several stages by a method he devised, and of which he proved the sufficiency. He was disposed to regard the existence of the grey suboxide,  $K_4O$ , of Berzelius as improbable, and he concluded that the intermediate products of oxidation were mixtures of  $K_2O$  and  $K_2O_2$  in variable proportion, depending on temperature and time and the nature of the oxidising medium. He compared these intermediate products with the successive stages in the oxidation of lead and with the several lead oxides described by various observers, the general nature of the change being similar. He obtained analytical numbers for the yellowish-green product which corresponded with the composition of a dioxide,  $K_2O_2$ , and described a number of reactions which appeared to indicate its individuality. He gained no certain proof of the existence of the trioxide,  $K_2O_3$ , but was inclined to regard the brownish-yellow stage of the colour change as some evidence of its formation. He states that "the more thoroughly the air is dried, the less is its oxidising action," as proved by Baker (*Phil. Trans.*, 1888), and subsequently by Holt and Sims (*T.*, 1894, **65**, 434), who showed that potassium may be distilled unaltered in perfectly dry oxygen.

Lupton's conclusions have been confirmed, in the main, by the last-named observers, although they found it impossible to associate the differences of colour with oxides of definite composition, the oxidation proceeding apparently without any break until the



heated mass consisted wholly of the bright orange-yellow peroxide,  $K_2O_4$ , described by Harcourt.

Holt and Sims also repeated Lupton's experiments on the action of the oxides of nitrogen on heated potassium, and with nitrous oxide obtained evidence of the formation of the buff-coloured trioxide and the sulphur-yellow dioxide, the existence of which in solution had already been established by Harcourt.

Lupton, in 1888, published a short communication in the *Proceedings* of the Society on compounds of chromium, and in 1891 he contributed to the *Philosophical Magazine* a controversial paper on "The Reduction of the Results of Experiments, with Special Reference to the Hydrate Theory of Solution" (*Phil. Mag.* [v], **31**, 418), which produced a rejoinder from Mr. Spencer Pickering.

Sydney Lupton was a painstaking and conscientious worker, scrupulously accurate, and a good manipulator, cautious in drawing conclusions or in forming opinions, but very tenacious in holding them when convinced of their soundness. His knowledge and, as his published work shows, his sympathies were almost exclusively confined to inorganic and physical chemistry; and owing probably to the limitations of his early training and his subsequent lack of opportunity, he never seemed to be attracted by the problems of modern organic chemistry.

As a fellow-townsmen and a member of the well-known Mill Hill Chapel, he was a great admirer of Joseph Priestley, who formerly ministered in Leeds, and began his chemical career there. At one time he conceived the idea of writing the life of the old philosopher and of bringing out an annotated edition of his complete works, for which he had gradually accumulated material. But to do justice to Priestley's astonishing versatility and the extraordinary range of his knowledge requires an equally exceptional man, and Lupton, after playing with the project for some time, finally relinquished it, being deterred from the attempt in all probability by its very magnitude. He was, however, well qualified to make it, especially as regards Priestley's scientific work and philosophical opinions, for he had considerable critical acumen and literary skill, was an omnivorous reader, and had extensive knowledge of the literature and science of the latter half of the eighteenth century.

On his removal to London, Lupton ceased to take any active part in experimental inquiry. He kept up his interest, however, in scientific work, was a frequent attendant at meetings of scientific societies, and at the lectures of the Royal Institution. He also interested himself in Bedford College, and in the work of St.

George's Hospital, and was for a time a member of its Committee of Management.

He was, perhaps, most generally known by his books on "Elementary Chemical Arithmetic" and "Numerical Tables and Constants in Elementary Science," published by Macmillan's, and based probably on his experience in science teaching at Harrow. His last production was a little book of some 120 small 8vo pages bearing the modest title, "Notes on Observations, being an Outline of the Methods used for determining the Meaning and Value of Quantitative Observations and Experiments in Physics and Chemistry, and for reducing the Results obtained." Notwithstanding the somewhat archaic ring of its title, it is an admirable piece of work, and well worthy of careful study by all engaged in quantitative work. In spite of its diminutive size, it must have involved a wide range of reading, no small exercise of criticism, and considerable skill and thought in arrangement and condensation. It shows Lupton at his best. It is a model of clear, restrained statement and rigorous logic, and should find a place in every physical and chemical laboratory.

At all periods of his life, Lupton was fond of travel, and his ample means made it easy for him to make extensive journeys. He was an acute observer and a shrewd judge of character, with a keen sense of humour—qualities which, added to his wide reading and knowledge of history and his readiness to communicate his knowledge, made him interesting as a companion.

He died at his London house, 102, Park Street, Grosvenor Square, on July 10th, 1918, and was buried at St. John's Cemetery, Roundhay. He showed his interest in the work of the Chemical Society by bequeathing to it his valuable chemical library.

T. E. THORPE.

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### GEORGE MARTINEAU, C.B.

BORN 1835; DIED FEBRUARY 5TH, 1919.

By the death of Mr. George Martineau, which occurred after a brief illness at his residence, Gomshall Lodge, Gomshall, Surrey, we have lost a member of an old and distinguished family and a man who was perhaps the greatest authority of his time in this country on sugar from its economic point of view. The deceased was the son of Mr. George Martineau, of Tulse Hill, and grandson of Mr. David Martineau, who in 1797 established the sugar refining firm which, as David Martineau and Sons, was at one time the largest in London; it has remained in the family for more than a

century. The fact is not without interest to our Fellows that this firm was one of the first, probably the first, in this country to recognise the value of scientific control, and the partners appointed the late Mr. C. Haughton Gill, F.C.S., first as their chemist and subsequently as their manager.

Mr. Martineau was educated at University College, London, and on coming of age entered his father's business, in which he was actively associated until his retirement in 1896. His connexion with sugar refining was on the commercial side, but he always took a keen interest in the general technology of the industry. Although a Liberal of the Gladstonian school, he recognised the defects of our fiscal system more than forty years ago; and in 1872, when the effects of the foreign sugar bounties began to make themselves felt, the British refiners appointed a Committee with Mr. Martineau as Secretary. This Committee visited the principal beet-growing countries of Europe. Thus commenced the anti-bounty campaign, which culminated in the abolition of the bounties by the International Convention of 1902. In recognition of his services, Mr. Martineau was appointed a Companion of the Bath by King Edward VII.

Inbued with the true scientific spirit, Mr. Martineau possessed a thoroughly logical mind, clearly shown by his numerous writings, which were continued up to the last days of his life: it may be said, indeed, that he died in harness. He was a chemist by instinct, and few commercial men had a greater appreciation of chemistry and chemical research. Keeping himself *au courant* with all the chief events in the progress of our branch of science, it was doubtless with this object that he became a Fellow of the Chemical Society in 1871. It cannot be forgotten that, equally with those members of his firm connected with the practical side of sugar refining, he shared a strong belief in the precise methods which chemical analysis affords when applied to commercial questions. In this connexion, we may point out that he was a pioneer in the establishment of the Beetroot Sugar Association of London, the functions of which were to check the weights and make analyses of the whole of the raw beetroot sugar shipped from the Continent to the Port of London.

Mr. Martineau's memory will be cherished by many. His charming personality, gifted conversational powers, wide erudition, and his deep sincerity had secured for him a wide circle of friends. Not a few have reason to be grateful to him for the assistance and encouragement he gave them at the commencement of their careers; but from these he resented open thanks, being quite content to view their progress with silent satisfaction.

ARTHUR R. LING.

## SIR ALEXANDER PEDLER, F.R.S.

BORN MAY 21ST, 1849; DIED MAY 13TH, 1918.

LIKE many other chemists who have attained an eminent position in the scientific world, Pedler began life in connexion with pharmacy. His father, Mr. George Stanbury Pedler, was in business as a pharmacist at 199, Fleet Street until, on the removal of old Temple Bar and the widening of Fleet Street, preparatory to the erection of the Law Courts, the premises were swept away.

Pedler received his early education in the City of London School, which he left at midsummer, 1865. In October of the following year, at the age of seventeen, he won a Bell Scholarship, and began work as a student in the laboratory of the Pharmaceutical Society in Bloomsbury Square. Here he went through the usual course of analytical work, and at the end of the session he was awarded a certificate of honour in practical chemistry. Before leaving, he began a piece of research suggested to him by the present writer, who was at that time Demonstrator in the laboratory. It was with great regret that he parted with the promising young student, who by this time had decided to leave the comparatively narrow field of pharmacy and proceeded to place himself under Professor (afterwards Sir Edward) Frankland, at the Royal College of Chemistry, then in Oxford Street. There, after carrying on his studies for two years further, he assisted Frankland in the separation of the amyl alcohols of fousel oil by Pasteur's process. This work was done in the laboratory of the Royal Institution, where Frankland had held the Professorship of Chemistry in succession to Faraday since 1863. From the optically active and inactive alcohols, Pedler prepared the corresponding valeric acids, and gave an account of his work to the Chemical Society in 1868 (*Journ. Chem. Soc.*, 21, 74). Further work in this direction was interrupted by his taking part in the solar eclipse expedition to Sicily in that year.

From 1871 Pedler served for two years as lecture demonstrator to Sir Edward Frankland in the Royal College of Chemistry in succession to Mr. Herbert McLeod, who had been appointed to the professorship of chemistry in the then newly instituted Royal Engineering College at Cooper's Hill. At the same time, he assisted in the research work on gaseous spectra in which Frankland and Lockyer were jointly occupied. This naturally directed Pedler's attention to the fascinating problems connected with the physical constitution of the sun and the stars. Consequently, on receiving

in 1873 appointment as professor of chemistry in the Presidency College, Calcutta, he naturally occupied himself with subjects connected with celestial chemistry, and soon after his arrival in India he was charged with special duty in connexion with the eclipse expedition of 1875.

On joining the Presidency College, he found that no practical work in any department of science was done by the students. To remedy this deficiency in the scheme of instruction was his first care, and ultimately he succeeded in securing the introduction of a small amount of practical work into the science course for the M.A. degree, and a practical examination was held for the first time in 1882. Ultimately, he had the satisfaction of finding the university regulations require every college sending up students to provide the necessary staff and appliances for teaching practically each of the departments of science, and each candidate for B.A. or B.Sc. degree to be examined practically.

Having been born in 1849, Pedler was still a very young man on reaching India, and those who knew him in his early days will gladly recall those features of his character which made him not only popular in youth, but, remaining unchanged to his latest years, contributed materially to his success in official life.

In India Pedler retained the professorship in Calcutta, together with the office of Meteorological Reporter to the Government of Bengal, for twenty-two years. He then became Principal of the Presidency College and Vice-Chancellor of the University. In 1899 he was appointed Minister of Public Instruction in Bengal, and became an additional Member of the Legislative Council under the Viceroy.

Among other institutions, Pedler took great interest in the Ravenshaw College at Cuttack, and was instrumental in obtaining accommodation for the physical and chemical departments in that institution. These successive steps in official life explain the fact that Pedler's original contributions to scientific chemical literature were limited to the one paper on valeric acids, already mentioned, and several which arose out of the circumstances of his residence in India.

Soon after his arrival in that country, he examined and reported on the coal-gas and water supplies of Calcutta. In 1878 he sent home a paper on the poison of the cobra, which was printed in the *Proceedings* of the Royal Society (27, 17).

In 1890 he contributed to the *Journal* of the Chemical Society three papers, which showed that he was utilising opportunities, previously neglected by chemists, of studying the action of tropical sunlight on chemical change. The first of these papers was entitled

"The Action of Light on Phosphorus and some of the Properties of Amorphous Phosphorus." The second paper was on "The Action of Chlorine on Water in the Light, and the Action of Light on certain Chlorine Acids." The third paper contained an account of attempts to estimate hydrogen sulphide and carbon bisulphide in gaseous mixtures by explosion with oxygen.

Pedler was a Fellow of the Institute of Chemistry and of the Chemical Society. He was elected F.R.S. in 1892. He was also an honorary member of the Pharmaceutical Society.

In recognition of his public services in India he was created C.I.E. in 1901, and on his return to England in 1906 he received the honour of knighthood. On his retirement he soon found occupation in public work; he became honorary secretary to the British Science Guild, which owes much to his devoted service, and on the outbreak of war he took up active duties connected with the research department of the Ministry of Munitions. Whilst attending a meeting of Committee at that office on Monday, May 13th, 1918, he was seized with sudden illness and expired immediately. His death came as a great shock and surprise to his many friends, among whom no suspicion of weakness had been entertained.

Pedler was twice married, first in 1878 to Elizabeth Margaret, daughter of C. K. Schmidt, of Frankfurt, and, secondly, to Mabel, youngest daughter of the late Mr. W. Warburton, R.N., of Dedham, who survives him. He left no children.

W. A. T.

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#### JOSEPH PRICE REMINGTON.

BORN MARCH 26TH, 1847; DIED JANUARY 1ST, 1918.

JOSEPH PRICE REMINGTON was born at Philadelphia on March 26th, 1847, and belonged to a well-known Quaker family, his ancestors having been for three generations members of the Society of Friends. His father, Dr. Isaac Remington, was a prominent Philadelphia physician, whilst his mother, the daughter of John Hart, was in a direct line of descent from an apothecary who practised his art in Philadelphia early in the eighteenth century. An inclination for the professional pursuit of pharmacy, which was manifested by Remington at an early age, would thus seem to have been inherited.

At the comparatively early age of fifteen years, Remington

suffered the loss by death of his father, and this appears to have affected his subsequent career; for a plan to supplement his preliminary education—obtained in private schools and in the high school at Philadelphia—by an academic course of study had to be abandoned. In 1863 he entered the establishment of Charles Ellis, Son and Co., a firm of wholesale druggists in Philadelphia, where he remained for four years, and during that time he attended evening lectures at the Philadelphia College of Pharmacy, from which he graduated in 1866. During the years from 1867 to 1870 Remington was employed in the manufacturing laboratories of Dr. E. R. Squibb, at Brooklyn, N.Y., and in this position he had exceptional opportunities for acquiring a knowledge of technical methods, especially in their application to chemical and pharmaceutical products, whilst also enjoying intimate association with a man who was widely known for his scientific attainments and exceedingly high ethical standards. Remington then returned to Philadelphia, and after a short period of service with the firm of Powers and Weightman, manufacturing chemists of that city, he established a pharmaceutical business on his own account, which was successfully conducted for thirteen years. In the meantime, he had also served as an assistant to Professor Parrish, and subsequently to Professor Procter, at the Philadelphia College of Pharmacy, and on the decease of the latter, in 1874, he was elected to the professorship of pharmacy in the college which had been his *alma mater*. The position which Mr. Remington was thus called on to fill he retained for the exceptionally long period of forty-four years, or until the close of his life, and during that time several thousand students had received instruction from him.

As circumstances did not permit Professor Remington to acquire a scientific training, in the modern sense, his attainments and talents were directed more to what may be termed the practical side of pharmacy and to editorial work. As examples of this activity, there may specially be noted his participation in several revisions of the "United States Dispensatory," the publication of his well-known text-book, entitled the "Practice of Pharmacy," and the arduous duties committed to him as Chairman of the Committee of Revision of the "United States Pharmacopœia."

Professor Remington was a Fellow of the Chemical, Linnean, and Royal Microscopical Societies of London, as well as an active member of several scientific societies in his own land. The esteem in which he was held by his professional colleagues had, moreover, been manifested by the bestowal of honorary membership in a large number of pharmaceutical organisations both at home and abroad. He had travelled widely in his own country, and had

several times visited Europe, the last occasion having been in the autumn of 1913, which will still be pleasantly remembered by many of his English friends.

The home life of Professor Remington, with a devoted wife and several children, was particularly happy. His genial nature and fluency as a speaker, together with the fund of interesting information which he possessed, rendered him a most pleasant companion. In social as well as professional circles he was therefore always gladly seen, and accorded a prominent place.

The writer of these lines is grateful for the privilege of rendering a slight tribute to the memory of one with whom a friendship had been sustained for more than forty years, and whose qualities of mind and heart had won such extended appreciation and regard.

F. B. POWER.

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### JEAN JACQUES THÉOPHILE SCHLOESING.

BORN JULY 9TH, 1824; DIED FEBRUARY 8TH, 1919.

ONE of the oldest and most distinguished of the foreign members of the Society, Jean Jacques Théophile Schloesing, passed away on February 8th of this year. He was in his ninety-fifth year, and almost all his life had been associated with agricultural chemistry. He knew its illustrious founders, Boussingault, Lawes, and Gilbert, when they were still young men almost at the beginning of their careers; he introduced new ideas at a critical stage, and, finally, when development had temporarily ceased, he opened up a new path, which is still leading to fruitful results.

Schloesing was born at Marseilles on July 9th, 1824. At the age of seventeen he entered the Polytechnic School, and left it two years later to take a post in the "Service des Manufacteurs d'Etat." He thus began his career at the most eventful period in the history of agricultural chemistry; it was the year, 1843, in which Lawes and Gilbert started their great work at Rothamsted, one year after Liebig's famous report on agricultural chemistry to the British Association, and four years after Boussingault had commenced his striking investigations at Bechelbronn.

He must have done well in his first post, for three years afterwards—in 1846—he became Director of the *École des Tabacs*, and within a few months published his first paper in the *Comptes rendus*; it was on nicotine and its estimation in leaf and manu-



factured tobacco. He was the first to obtain nicotine in any quantity; it had previously been prepared, as he tells us, only in "quelques rares échantillons." Schloesing verified its composition and designed a method for estimating it within about 1 per cent.—a very accurate determination for the time. The method consisted in displacing the nicotine with ammonia, extracting with ether, eliminating the excess of ammonia by the evaporation of the ether, and then titrating the residual base with sulphuric acid. For five years no further publications appeared, then followed an ingenious paper on the determination of ammonia in tobacco; milk of lime was added, and the mixture placed over sulphuric acid in the cold. The ammonia volatilised, and was absorbed by the acid, but at the low temperature of the experiment no decomposition of other substances occurred. This paper was followed shortly afterwards by one on the estimation of nitrates in presence of organic matter; hydrochloric acid and a ferrous salt were added, and nitric oxide produced; this was washed free from hydrochloric acid, then mixed with air or oxygen, converted into nitric acid, and titrated with an alkali. Subsequently, however, Schloesing found that conversion into nitric acid was unnecessary, and he designed a method for direct measurement of the nitric oxide. He also introduced considerable improvements into the methods for estimating ammonia in dilute liquids, such as rain. As an illustration of the very cumbersome nature of some of the methods then in vogue, it may be mentioned that the determination of ammonia in rain-water at Rothamsted, carried out in 1853, had involved the distillation of 2 cwt. of rain and evaporation of the distillate with sulphuric acid; in spite of all the laborious care bestowed on the work, the figure obtained was probably double the true value.

For the next seven years Schloesing published no scientific work, but from 1860 onwards he issued a number of important publications. In 1860, also, he began some cultural experiments with tobacco, which lasted for fifteen years, and were designed to ascertain whether the physical properties and nicotine content of the leaf are characteristic of the variety or the result of environmental factors. In the first series, tobacco was raised from samples of seed coming from various regions; the resulting leaf had in each case the physical characters and nicotine content characteristic of the parent plants grown in their original home. The second series was more extended and lasted fourteen years; its purpose was to discover whether any marked alteration occurred in the characteristic properties when a variety is cultivated in a new district. Havanna tobacco was grown, and the seed saved; some was sown and some was stored; each year a certain quantity of the seed of

each generation was sown. In no case was any difference observed.

In 1866 Schloesing began his investigations on the soil. It was probably in this subject more than in any other that the genius of the man shone out. Looking back at these papers, their striking feature is their modernness; one can well believe that at the time of publication they would not be fully appreciated. Again and again he broached new subjects, which neither he nor his contemporaries developed, but which later workers rediscovered thirty or forty years afterwards and showed to be of signal importance. He was essentially a pioneer rather than a builder, and he had the extraordinarily good fortune to discover gold almost every time; but he never himself developed his "finds," and the subject was not sufficiently well organised to ensure that others should develop them for him.

Schloesing's period of greatest activity was from 1866 to 1879, when he was between forty-two and fifty-five years of age; during this time he opened up no fewer than five new fields of soil investigation, three of which are now proving extremely valuable. His first soil paper was on the soil solution, which he separated from the solid particles by a displacement method. The subject received very little attention for nearly forty years; its importance was not fully realised until Whitney and Cameron in America published their striking paper in 1903, when investigations began again, using at first methods similar to those that Schloesing had designed. At the present time it receives perhaps more attention than any branch of soil chemistry.

Another subject which has come into prominence in recent times was investigated by him in 1868. He showed that nitrates are decomposed during certain fermentations, and five years later he further showed that they are reducible to gaseous nitrogen in soils deprived of oxygen. He also demonstrated that oxidations rather than reductions are the normal phenomena in soils under natural conditions; surface soils readily absorb oxygen, whilst sub-soils do not. After a lapse of nearly thirty years this phenomenon was independently rediscovered, and its investigation figures prominently in some of the most recent research programmes.

His most important work, however, was on nitrification. For a long time it had been known that nitrates are gradually formed when plant or animal residues, farmyard manure, etc., are incorporated in the soil. The process was of much technical importance in the seventeenth and eighteenth centuries as the source of nitrates for gunpowder. During the Thirty Years' War and other great continental wars, the various governments had been seriously

concerned in these so-called nitre beds, and had done a great deal to stimulate their development. An interesting collection of memoirs relating to the practical details was published in Paris in 1776.\* A study of these papers shows that the conditions of the change were tolerably well ascertained even then, but nothing was known of its mechanism.

It has several times happened in the history of civilisation that agriculture has benefited by knowledge gained during war. The mass of information accumulated during the eighteenth century wars, and apparently rendered useless in the nineteenth century by the promise of peace and the discovery of nitrates in Chile, was found to be of fundamental importance in agriculture. Boussingault had realised, and Schloesing at once accepted the view, that the nutrition of plants, so far as nitrogen was concerned, depended on the nitre-bed processes; organic nitrogen compounds, useless as plant nutrients, became converted into highly valuable nitrates when added to the soil; the more rapidly this change could be brought about, the better for the plant. So long, however, as the mechanism of the change was unknown, the old knowledge was simply empirical and incapable of full utilisation. Many investigations had been made, but the problem remained unsolved. The balance of opinion was in favour of a purely physical process, but there was also a strongly supported chemical hypothesis.

In 1875 a Commission was appointed to inquire into a scheme for carrying Paris sewage out to the land between Clichy and the forest of St. Germain, and Schloesing was asked to draw up the report. Rarely, even in France, can an essentially practical inquiry have led to such striking scientific results. When Schloesing had finished the investigation, he had not only discovered a new and vastly improved method of treating sewage, but he had realised what was the cause of nitrification, and thus founded the science of soil bacteriology. We cannot do better than let him tell the story in his own words:

"I was selected," he tells us, "to draw up the report of this Commission. On this occasion, following the plan indicated in 1856 by M. Hervé Mangon, and taking advantage also of the more recent investigations of Dr. Frankland, I endeavoured to elucidate the principles involved in the land treatment of sewage by connecting the process with the phenomena of slow combustion of organic matter in an atmosphere containing oxygen; I investigated at the same time the conditions necessary to secure satisfactory

\* "Receuil de Mémoires et d'Observations sur la formation et sur la fabrication du Salpêtre par les Commissionnaires nommés par l'Académie pour le jugement du Prix du Salpêtre."—Paris, 1776.

purification in practice. I made a special point of distinguishing two problems which were often confused: purification simply and solely of Paris sewage, which would only require an area of 2000 hectares (5000 acres), and agricultural utilisation of Paris sewage, which would require an area twenty times as great.

"Boussingault had just published the researches on nitrification that he had carried out some time previously. Blood, meat, wool, straw, and oil-cake did not nitrify when mixed with sand and chalk and allowed slowly to oxidise, but they rapidly nitrified when mixed with soil. I had vainly tried to nitrify ammonia by adding it to sand and chalk and leaving the mixture exposed to air. These results led me to think that the property of bringing about nitrification was peculiar to soil.

"Wishing to fix my ideas on the subject, I made the following experiment. A large tube, 1 metre long, was filled with 5 kg. of ignited sand mixed with 100 grams of powdered chalk. The sand was watered daily with sewage, the amount being so arranged that it took eight days to traverse the tube. For the first twenty days there was no sign of nitrification, then nitrates began to appear, and the amount rapidly increased; finally, the liquid flowing out of the tube contained neither ammonia nor organic matter—the sewage was absolutely purified."

The quality of the man's genius was revealed in two striking deductions drawn from this simple experiment. One was of supreme practical importance, and has revolutionised sewage disposal practice.

"Au point de vue de l'épuration des eaux d'égout, l'expérience . . . prouve, en effet, qu'il n'est nullement nécessaire que l'irrigation soit établie sur les terrains agricoles; de sables stériles se prêtent parfaitement à l'épuration, lorsque le ferment nitrique, apporté par les eaux mêmes, a pris possession du milieu."

From this to the modern bacteria bed is no great step, at any rate in principle.

The second deduction was of even greater consequence for the development of agricultural science. Reverting to the delay of twenty days in the setting in of nitrification, Schloesing and Muntz asked why it set in. With characteristic shrewdness they observed that this delay could scarcely arise if the process were purely physical or chemical; some biological factor seemed to be indicated. In order to test this possibility they added a little chloroform to the sewage; nitrification at once stopped. They then removed the chloroform and "seeded" with a little fresh sewage; after an interval nitrification began again. This showed that the process was brought about by living organisms, and forthwith Schloesing

and Muntz announced the existence of a living ferment. The discovery at once attracted attention; Warington at Rothamsted immediately recognised its importance, and proceeded to investigate nitrification in the Rothamsted soils; he was able to confirm the accuracy of Schloesing's deductions. Later on, the proof was made more rigid by Winogradsky's discovery of the organism. It is no diminution of the credit of the discovery that Pasteur in 1862 had already foreshadowed it, as Schloesing himself pointed out, in his remarkable statement:

"Beaucoup d'êtres inférieurs ont la propriété de transporter l'oxygène de l'air, en quantité considérable, sur les matières organiques complexes: c'est un des moyens dont se sert la nature pour transformer en eau, acide carbonique, oxyde de carbon, azote, acide nitrique, ammoniacque, les éléments des substances organiques élaborées sur l'influence de la vie."

This research marks the beginning of soil bacteriology. It seized the imagination of the younger workers, and speedily attracted recruits to the new subject. Although Schloesing did not himself develop the subject, he was satisfied that the "ferment nitrique" did not exhaust the list of soil organisms. Reverting to his earlier work on the absorption of oxygen by soils, he says in one of his lectures\*: "C'était là, pensait-on alors, un fait purement chimique. On sait aujourd'hui que c'est principalement un fait biologique, c'est-à-dire que la combustion observée est le résultat de la vie de nombreux organismes, tel par exemple que le ferment nitrique, lequel est chargé de transporter l'oxygène sur l'azote."

These investigations by no means represent the whole of his work on soil, although they may well prove to be his most permanent contributions to science.

By a lengthy washing process, he obtained a preparation of the finest clay particles which remained indefinitely suspended in pure water, but was precipitated by traces of a calcium or magnesium salt. This was commonly regarded as being in some sense the essential clay, and agricultural chemists marvelled at the minute amount present even in heavy soils. The conception served a useful purpose, but it has since been replaced by a broader one: the soil is now considered to be made up of particles varying from 1 mm. downwards to molecular dimensions, the different groups merging one into another without perceptible breaks. The clay group is assigned for convenience an upper limit of 0.002 mm., but this is regarded as purely conventional.

Another important investigation had to do with the movements of calcium carbonate in the soil. The conditions of solubility of

\* "Leçons de chimie agricole," 1883.

calcium carbonate in carbonic acid were determined, and the relationship between the quantities of these two substances was shown to follow a logarithmic law. Deductions were drawn which threw important light on the practice of liming and marling, and on the presence of lime in natural waters.

During the course of these investigations, Schloesing was appointed in 1876 to the Chair of Agricultural Chemistry in the Institut Agronomique, then just founded. Eleven years later, in 1887, he followed the illustrious Boussingault at the Conservatoire des Arts et Métiers. During his active period, his lectures were collected by his son in a volume, which still remains a source of inspiration to the student.

In 1875 he began another important group of investigations: he carried out a series of determinations of the amount of ammonia in the air, and published some interesting speculations as to its source. He supposed that a great natural circulation took place; the nitrates washed out from the soil find their way to streams and rivers, and finally to the sea; there they are reduced to ammonia, some of which escapes into the atmosphere, is blown over the land, and there absorbed by the soil or washed down by the rain. The ammonia then nitrifies, and such of the resulting nitrate as is washed out from the soil by rain-water passes once more through the same cycle.

In like manner, he supposed a circulation of carbon dioxide between oceans and atmosphere, and in this way he explained the smallness of the variations in amount of the carbon dioxide in the air from time to time. He considered that the proportion of carbon dioxide in the air was probably diminishing, although, of course, very slowly. "What," he asked, "will be the result?"

"Cet appauvrissement continue-t-il encore, et, s'il en est ainsi, ira-t-il jusqu'au point où il causerait la ruine de la végétation et par suite la fin de toute vie à la surface de la terre? La solution de cet problème d'un si haut intérêt nous échappe absolument. Elle ne pourra être donnée que par les générations qui viendront longtemps après nous."

Well may we envy a man and a generation that had nothing worse to worry about!

E. J. RUSSELL.

## ALFRED SENIER.

BORN JANUARY 24TH, 1853; DIED JUNE 29TH, 1918.

## I.

ALFRED SENIER was born on January 24th, 1853, at Burnley, in Lancashire. His father, who had been one of the early settlers in Dover, Wisconsin, had returned to England some six years previously to engage in business as a pharmacist, but for reasons of health he found it necessary to return to America shortly after the birth of Alfred, his eldest son. Thus except for a brief visit to England during infancy and another during his student days, Senier's whole youth up to the time of his graduation as M.D. at the University of Michigan in 1874 was spent in the United States, chiefly at Mazomanie. Mr. Alfred Senier, the father, appears to have been a man of romantic disposition, which found its expression in a certain restlessness, leading him in early life to spend several years at sea and later to travel considerably in Europe. The son inherited this taste for travel, and was allowed to visit both London and Paris at the age of eighteen in the middle of his student career.

Immediately after his graduation the family finally returned to London, where Senier obtained a post at the school of the Pharmaceutical Society, first as assistant to Prof. Attfield and later as demonstrator. He was elected a Fellow of the Chemical Society in 1875 and a Fellow of the Institute of Chemistry three years later.

In 1881 he left the school of the Pharmaceutical Society in order to take charge of the chemistry teaching at St. John's College, Battersea, where he remained for three years.

During this period in London his interests extended beyond his professional duties, which hitherto did not seem to offer him sufficient scope for his mental activities. Endowed as he was with the faculty of accurate reasoning, and with clearness and breadth of mental vision, his interest at this time turned markedly to philosophical questions. We find him appointed as honorary secretary and treasurer of the Aristotelian Society on April 19th, 1880, when it was first organised. He acted in this capacity until 1884, and in 1902 he was elected an honorary life member. At its fifth meeting he delivered a lecture to the Society on "Plato." In 1882 we find him delivering a series of lectures on the "Elements and Early History of Terrestrial Physics" to the Positivist Society in Newton Hall, Fetter Lane. It is also interesting to observe that he wrote to the *Pharmaceutical Journal* in 1877 a spirited letter in

support of the proposal to admit lady pharmacists into the Pharmaceutical Society.

In 1884 he left London for Berlin, where he studied chemistry under A. W. von Hofmann. It was at this period of his life that he received his greatest inspiration. Enthusiastic and imaginative by nature, he threw himself wholeheartedly into his work, and soon attracted the attention of Hofmann, who became his ideal as a professor, lecturer, and teacher. A close friendship bound him to his old master, in whose family circle he spent many happy evenings, and whose personality made a lasting impression on his mind.

Later in life when fulfilling his duties in an academic chair he loved to think that the same happy relations existed between his students and himself as he had felt when a student of Hofmann. His interest in his past students never flagged. He was ever ready to help them, and always pleased to hear of their success.

Senier's own exceptional powers as a teacher were no doubt due to a large extent to the powerful influence of Hofmann, of whom he was never tired of speaking. Among his papers this idea is expressed in words thus: "I had special opportunities for studying the methods of teaching for which Hofmann was justly famous. He possessed that rare gift of inspiring his students with the discoverer's enthusiasm. We discovered, with him to lead us, things known to science; and then, without realising a difference, we followed him to things that were new, and thus became chemists with the habit of research. With such a leader in research, with such a teacher in the right meaning of the word, no wonder that those who came within his influence became inquirers and teachers too."

On June 25th, 1887, he graduated Ph.D. in Berlin, and returned shortly afterwards to London.

Here he remained for a few years writing articles for the standard dictionaries of chemistry until he was called to act as locum tenens for Maxwell Simpson, Professor of Chemistry at Queen's College, Cork, in 1890. The latter resigned the following year, and was succeeded by Prof. A. E. Dixon, of Galway. The vacancy thus created was filled by the appointment of Senier to the Chair of Chemistry at Galway, which he occupied until his death.

This Chair when first established in 1849 was filled by Edmund Ronalds, who in the early days of the Chemical Society served as Secretary and also acted as Editor of this Journal.

In addition to fulfilling the duties as Professor of Chemistry at Queen's College, Galway, Senier acted as Lecturer in Medical Jurisprudence and Hygiene.

In Galway his professorial duties, his work on the College Coun-



cil, and his personal interest in his students engaged his closest attention. His strong personality and buoyant enthusiasm made a powerful appeal to the minds of his students, with whom he was always immensely popular. He was a champion of students' interests, and never tired of reminding them that he was, and would remain, "always a student." Although not naturally attracted to athletic sports, he quickly realised their healthy influence and value in promoting *esprit de corps* and harmony among young men, assembled from all parts of Ireland, from homes representing all shades of religious and political differences. They sought and obtained in Galway a University training under a system which, although technically non-residential, was by reason of the smallness and isolation of the "Citie of the Tribes" virtually residential. Senier seized his opportunity and quickly won the affection of all the students by becoming the active patron of their sports. He founded the athletic union and acted as its president and treasurer for seventeen years. The astonishing prowess of the football team in its competitions with the larger sister colleges of Belfast and Cork was in no small measure due to his sympathetic and generous support.

Meanwhile, the problem of continuing his researches had to be faced, and was tackled courageously and successfully. At first little progress could be made, as Galway offered but a poor field for creating and maintaining an advanced chemical atmosphere. Nevertheless, he persisted in his attempt, and soon acquired a good chemical library and equipment sufficient to make a start. Well-furnished modern laboratories soon followed, and in conjunction with various assistants, demonstrators, and senior students he was eventually able to contribute a large number of papers, chiefly on acridines and on phototropic and thermotropic compounds, to the *Transactions* of this Society.

In 1908 the Royal University of Ireland conferred on him the degree of D.Sc. *honoris causa*. This event was made the occasion of a public presentation to him of an address and silver casket from his old students, whose eager and liberal response, even from the most distant parts of the world, bore ample testimony to the lasting feeling of reverence and goodwill in which they held their old teacher and patron of their sports.

He was elected a member of the Royal Irish Academy, and in 1912 he acted as President of the Chemical Section of the British Association at the Dundee Meeting.

When the National University of Ireland was created in 1908 he took an active part in its organisation and development. He was

a member of the Senate until his death, which took place on June 29th, 1918, in Galway after a brief illness. Senier married in 1887, and is survived by his wife and two daughters.

W. S. M.

## II.

By the death of Alfred Senier the country has lost one of its most enthusiastic and devoted workers in the domain of organic chemistry. The loss is felt most keenly by all his students and co-workers, who will always cherish the remembrance of his sympathetic and inspiring personality. In him the spirit of scientific inquiry was strong indeed, for in the face of difficulties, which would have baffled and beaten many a man of less sterling worth, his courage never failed, but enabled him to pursue unwearyingly the lofty ideals which he had formed in his youth and to achieve a measure of success and distinction which will assuredly become fruitful in the future.

Even before leaving America he had shown evidence of a desire to undertake original investigations, his first paper, on the analysis of soap, appearing in the *American Journal of Pharmacy* in 1874. At the School of the Pharmaceutical Society his aspirations received encouragement from Prof. Attfield, and he contributed a series of articles to the *Pharmaceutical Journal*, chiefly relating to the investigation of pharmaceutical preparations and including a table for the qualitative analysis of scale preparations, alkaloids, etc. The interaction of glycerol and borax particularly engaged his attention, because he found that he could utilise it as a means for detecting glycerol. In 1878 he contributed to the *Transactions* of the Chemical Society "A New Test for Glycerin." He also published a number of articles in the *Sanitary Engineer*.

In Berlin Senier came under the powerful influence of A. W. von Hofmann. The enthusiasm which Hofmann aroused in him remained with him to the end, and he spoke of him almost with veneration in his public lectures.

Inspired as he was by his experience in Germany, the whole course of Senier's later life afforded abundant evidence that he had learned nothing of the modern German aggressive spirit of world-domination. Indeed, his realisation of its existence only came to him after war was declared, and its effect on him was painful in the extreme, as shown in his letters to the writer.

In Berlin his attention was first directed to the action of heat on the formyl and thioformyl derivatives of aromatic amines, and later to the investigation of cyanuric acid and cyanuric chloride. He was

able to show that the alleged  $\alpha$ - and  $\beta$ -isomerides obtained by Herzig by the interaction of carbamide and hexabromoacetone were in reality identical with ordinary cyanuric acid. This work was embodied in his dissertation for the degree of Ph.D.

Shortly after his appointment to Galway he reverted to the examination of cyanuric acid, and found that the white solid produced by the polymerisation at  $0^{\circ}$  of freshly distilled cyanic acid was not pure cyamelide as was supposed, but consisted chiefly of cyanuric acid mixed with 30 per cent. of cyamelide.

Being greatly interested in all Hofmann's work, he decided to follow up the reaction by which ethylenediamines and piperazines are formed from arylamines. By using methylene dihaloids instead of ethylene dihaloids, he found that although the simplest arylamines give rise to methylenediamines, as the molecules increase in complexity through the inclusion of methyl groups or of condensed rings, the character of the reaction changes and results in the formation of acridines. Thus from  $\psi$ -cumidine he obtained hexamethylacridine, and from  $\alpha$ -naphthylamine a new dinaphthacridine. This result led him to study the subject of acridines in some detail, and a series of papers appeared in the *Transactions*. He also introduced a new and convenient system of notation in the acridine series. This work was followed by a paper on quinazolines and a series of papers on the synthesis of phototropic compounds, to which he was led by his observations on salicylidene-*m*-toluidine during the course of his investigations on acridines. This discovery of phototropic change led him to prepare and examine a large number of similarly constituted anils, many of which were also phototropic, although the property was by no means characteristic of the class. The change from the paler variety to the darker under the influence of sunlight occurs rapidly in a few minutes—whereas the reverse change requires a much longer time. This process of reversal can, he found, be accelerated by raising the temperatures, but there appears to be for each substance a critical temperature above which the property of phototropic change disappears. In some cases this temperature is near the melting point; in others it is much lower; in fact, in the case of two compounds examined, namely, salicylidene-*p*-anisidine and 2-hydroxy-3-methoxybenzylidene-*p*-xylylidine, no phototropic change is observed until a temperature of  $-20^{\circ}$  is reached. Similar colour changes were observed to take place under the influence of heat instead of light, this phenomenon being termed *thermotropy* by Senier. Thermotropy appears to be much commoner than phototropy, and in many instances the thermotropes were also found to be phototropic. The suggestion was put forward by Senier that these phototropic and thermotropic

changes are to be ascribed to isomeric changes affecting the aggregation of molecules in solids rather than to changes in the structures of the molecules themselves. In his Presidential address to Section B of the Dundee meeting of the British Association in 1912 he developed this idea of the existence of solid molecular aggregates. Several instances of polymorphic changes due to trituration were also examined, chiefly in the case of *p*-hydroxybenzylidenearylamines. This work, extending over several years, was the subject of a series of papers in the *Transactions*, and remains unfinished. No doubt it will be possible in the future to throw more light on the subject by means of optical measurements.

Apart from his purely scientific studies, Senier took a deep interest in educational affairs. The difficulties which had to be encountered in Galway were due partly to the remoteness of the College from the main centre of scientific activity and partly to the anomalous character of the College during the greater part of Senier's life in Galway.

Since the dissolution of the Queen's University in 1879 the three Colleges at Belfast, Galway, and Cork had been reduced from the status of integral members of a university to that of colleges where students were able to study for the examinations of an external institution—the Royal University. In addition to this loss of prestige, the College at Galway suffered through lack of active support by the people of Connaught. It was therefore not in close sympathy with its environment. This state of affairs has happily been remedied by the abolition of the Royal University and the creation in 1908 of two new teaching universities, namely, the National University of Ireland and the Queen's University of Belfast. The College at Galway, re-named "University College, Galway," became a constituent part of the National University, and Senier was elected to a seat on the Senate. The existence of the College has often been threatened, but it has survived and, indeed, attained a flourishing condition. There is no doubt that Senier's efforts to foster the spirit of scientific research materially advanced the cause of education in Galway and in Ireland. In his public lectures on "A Visit to Giessen; or Thoughts on Liebig and Chemistry in Germany" and "Bonn on the Rhine; Pages from its History and Stray Thoughts on Education" he deals in a very attractive way with the history of the development of scientific research in Germany, and in his lecture before the Royal Dublin Society in 1910 on "The University and Technical Training" he made a very lucid and careful analysis of the various university systems in the world. In view of modern needs these essays\* are

\* Published at Dublin, 1910, by Edward Ponsonby, 116, Grafton Street.

well worth reading, for he explains very clearly how industrial development does not depend on the technical education of the operatives, but arises naturally from the development of the highest form of scientific activity at the universities.

P. C. AUSTIN.

### JOHN BISHOP TINGLE.

BORN 1867; DIED AUGUST 5TH, 1918.

JOHN BISHOP TINGLE, Professor of Chemistry in McMaster University, Toronto, who died on August 5th, 1918, at the age of fifty-one, after a brief illness, received his early training at the Royal Grammar School, Sheffield, entering Owen's College, Manchester, in 1884, under the late Sir Henry Roscoe. In 1887 he proceeded to the University of Munich to study with Claisen and von Baeyer, where he took the degree of Doctor of Philosophy in 1889. While at Munich his studies were essentially in organic chemistry, his dissertation for the degree dealing with the action of ethyl oxalate on aliphatic ketones.

On returning to England Dr. Tingle held certain junior appointments which offered him opportunities for research. Owing, however, to unforeseen family responsibilities he was compelled to give up, for a time, his chosen career of investigation, and taught chemistry in secondary schools.

In 1896 he came to America and was successively professor of chemistry at the Lewis Institute, Chicago (1897-1901), Illinois College, Jacksonville (1901-1904), and assistant in charge of organic chemistry at Johns Hopkins University under Professor Remsen (1904-1907). During his residence in the United States Dr. Tingle became sub-editor and abstractor in organic chemistry on the staff of the *American Chemical Journal*, his work being characterised with care and precision, and as his study of current literature in his chosen field was extensive and exhaustive he spared no pains to make his abstracts clear, complete, and useful. His long training as an abstractor on the staff of the *Journal of the Chemical Society* specially qualified him to take this important part in organising the organic abstracts for the American journal.

Dr. Tingle was appointed professor of chemistry at McMaster University, Toronto, in 1907, in which post he laboured energetically and faithfully until his death. It was perhaps in teaching, for which he possessed a special talent, that Dr. Tingle did his best

and most valuable work for the country of his adoption. He was insistent on the importance of careful, accurate, and clean craftsmanship, and held that theory was useless and often misleading without a knowledge of how it had been deduced and how it could be applied in practice. He laid special stress on the need of manipulative skill of the highest order as a necessary pre-requisite to orderly and clear reasoning and successful results.

Dr. Tingle's original work, embodied in upwards of thirty publications, deals with problems of organic chemistry, and is centred chiefly round the mechanism of the "Claisen reactions" and the products and mechanism of nitration in the benzene series. His last paper, which did not appear in print until after his death, settled certain minor points previously undetermined, and was intended to clear the way for a comprehensive study of the laws governing nitration and the means by which their reactions could be controlled. Dr. Tingle made organic research his life work, and carried through to a successful issue a large number of investigations in his chosen field. He held a first place among organic chemists in Canada, and had he been spared it was expected that he would have been able in a few years to devote himself almost exclusively to research. Much has been lost by his death.

In the sphere of Canadian war work Dr. Tingle was the first to recommend the intensive training of girls for employment in munition and chemical factories in Canada, and laid himself out energetically to instruct them towards this end. The extra work involved undoubtedly accelerated his death.

He translated and edited several important works in chemistry. For a long time "Spectrum Analysis," by Landauer and Tingle, was the most comprehensive work on the subject in English.

Dr. Tingle was a kind and generous man, taking a great personal interest in his students and their work and exciting their ambition and enthusiasm for advanced study.

He leaves a widow and two children.

W. R. L.

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XXXIV.—*Porphyroxine.*

By JITENDRA NATH RAKSHIT.

THE ethereal extract obtained in the estimation of morphine in opium by the process described by the author (*Analyst*, 1918, **42**, 320) left a viscid, brown, crystalline residue on evaporation, which when dissolved in dilute acid always gave a solution, becoming more and more purple on stirring or heating. Previous authors do not agree regarding the composition of this colouring matter; Merck, in 1837, prepared from opium a substance containing its colouring matter, and called it porphyroxine; Hesse remarked (*Annalen*, 1870, **153**, 47) that the substance prepared by the former investigator was a mixture of several alkaloids, one of which is meconidine and another probably rhœadine. The same author (*Annalen, Suppl.*, 1864—1865, **4**, 50) noted that Merck's porphyroxine agrees with rhœadine in method of preparation, properties, and composition. It was thought desirable to investigate whether there is any alkaloid that may be correctly called porphyroxine in Indian opium. The alkaloid now isolated was very likely a constituent of what Dey (*Pharm. J.*, 1882, [iii], **12**, 397) obtained on evaporation of the ethereal extract prepared by shaking an aqueous solution of opium made alkaline with sodium carbonate or ammonia, and apparently also of what Merck called porphyroxine. Considering these facts and that the alkaloid gives a purple solution with dilute acids resembling porphyrin, the name porphyroxine may reasonably be retained.

The alkaloid isolated is fairly readily soluble in water, in which respect only it resembles papaverine, codamine, narceine, and codeine, but its other properties are in striking contrast with them; the solutions of the base or its salts are strongly levorotatory, it does not sublime like codamine, and, unlike codeine, the aqueous solution of its hydrochloride gives a white or pale yellow precipitate with ammonia.

*Preparation.*—Twenty parts of Indian opium powder and nine parts of freshly slaked lime were triturated in a mortar for five minutes, then 100 parts of water were added gradually during one hour, the trituration being continued. The solution was filtered and the filtrate shaken with an equal bulk of ether for ten minutes in a separator. The ethereal layer was then filtered into another separator containing some dry lumps of calcium chloride, shaken for five minutes, allowed to settle, the ethereal solution decanted, filtered, and evaporated on a water-bath. A pale yellowish-brown,

soft, crystalline residue was obtained, which when rubbed with a spatula on a porcelain plate for three to four hours became a dry powder. One hundred grams of this powder were heated with 200 c.c. of light petroleum until the solvent boiled briskly, the whole was shaken for fifteen minutes, heated again to boiling, and the petroleum decanted as completely as possible, the insoluble residue being carefully excluded. This process of extraction was repeated five times, 100 c.c. of petroleum being used each time, and finally the contents of the flask were collected, dried, and powdered. Ten grams of this powder were triturated with 100 c.c. of 10 per cent. hydrochloric acid gradually added during half an hour, and then with 100 c.c. of water gradually added during another hour, and filtered quickly, the residue being washed with a little dilute hydrochloric acid. To the filtrate was added a saturated solution of sodium hydrogen carbonate, a thin layer of ether being kept on the surface of the liquid, and the latter was stirred until the addition of a further quantity did not produce any effervescence. After remaining for half an hour for the complete separation of the precipitate, this was collected and washed with distilled water. The filtrate, measuring about 500 c.c., was shaken with 50 c.c. of chloroform for fifteen minutes, the chloroform removed, and the process of extraction was similarly repeated thrice with 30, 25, and 25 c.c. of chloroform respectively. The chloroform extracts were mixed together, filtered, the bulk of the solvent was distilled off, and the residue dried slowly on the water-bath; it was then kept overnight in a desiccator. Sometimes the substance formed a soft, viscid, crystalline mass, but generally a pale brownish-yellow, viscid varnish, which on rubbing with a spatula against the side of the basin for an hour became a crystalline, pink powder. Five grams of this powder were heated on a water-bath with 100 c.c. of light petroleum (b. p. 100—120°) just to boiling, the mixture was then shaken for fifteen minutes with a rotatory motion, heated again to boiling, and the petroleum decanted through filter paper, the undissolved residue being carefully excluded. The residue in the flask was again twice extracted similarly with 80 and 60 c.c., respectively, of light petroleum, care being always taken not to melt the substance, thus causing the extraction to be incomplete. The successive petroleum extracts were collected and allowed to evaporate, when the base crystallised in groups of radiating, shining, pale yellow prisms, which were carefully separated from a thin film of non-crystalline residue, powdered, and dried in a desiccator. Several samples from different preparations were analysed, the results of one only being given below:



0.2950 gave 0.7530  $\text{CO}_2$  and 0.1854  $\text{H}_2\text{O}$ .  $\text{C}=69.46$ ;  $\text{H}=6.98$ .  
 0.253 „ 10.6 c.c.  $\text{N}_2$  (moist) at  $34^\circ$  and 750 mm.  $\text{N}=4.36$ .  
 $\text{C}_{19}\text{H}_{23}\text{O}_4\text{N}$  requires  $\text{H}=6.99$ ;  $\text{C}=69.30$ ;  $\text{N}=4.26$  per cent.

Porphyroxine forms pale yellow or white, transparent prisms melting at  $134\text{--}135^\circ$  to a clear, transparent, straw-coloured liquid which solidifies on cooling. It is a non-deliquescent substance appreciably soluble in water, giving a strongly alkaline solution; it is readily soluble in dilute acids, acetone, carbon disulphide, chloroform, or glacial acetic acid, moderately so in benzene, carbon tetrachloride, methyl or ethyl alcohol, toluene, or ethyl acetate, sparingly so in amyl alcohol, ether, light petroleum, ammonia, or barium hydroxide, and almost insoluble in aqueous sodium hydroxide, potassium hydroxide, or lime water. When its dilute mineral acid solutions are kept exposed to air, they assume a fine pink porphyrin colour. The base has a strongly alkaline reaction towards cochineal, methyl-orange, and litmus, but has no action on phenolphthalein. Iodine solution gives an orange precipitate with the aqueous solution of the base and a brick-red precipitate with its dilute hydrochloric acid solution. Mayer's reagent gives a white precipitate with its aqueous solution and the usual pale yellow one with its dilute hydrochloric acid solution. Colour reactions of the base are often vitiated by the presence of a small quantity of impurity, and the following reactions were observed with a sample specially prepared by recrystallising three times from petroleum. It gives a red colour with concentrated sulphuric acid, a grass-green with concentrated sulphuric acid and a small quantity of potassium dichromate, a pale yellow with concentrated nitric acid, and an orange with concentrated hydrochloric acid; a brownish-red precipitate is obtained on adding ferric chloride to its sulphuric acid solution, and when fused with potassium hydroxide it becomes brown and gives off a strongly alkaline vapour without becoming charred.

0.2540, made up to 50 c.c. with chloroform, gave  $\alpha-4.1^\circ$  (Ventzke) in a 2-dcm. tube at  $32^\circ$ , whence  $[\alpha] -139.9^\circ$ .

The *hydrochloride* crystallises from water in prismatic needles. It is a stable salt, and, on heating, softens at  $140^\circ$  and melts at  $155^\circ$  to a clear, pale yellow liquid which does not solidify quickly on cooling:

0.1168 gave 0.0460  $\text{AgCl}$ .  $\text{Cl}=9.7$ .

$\text{C}_{19}\text{H}_{23}\text{O}_4\text{N}\cdot\text{HCl}$  requires  $\text{Cl}=9.7$  per cent.

It is a non-deliquescent, crystalline, stable substance readily soluble in water, chloroform, methyl or ethyl alcohol, or glacial acetic acid, sparingly so in amyl alcohol or carbon disulphide, and

almost insoluble in acetone, benzene, carbon tetrachloride, ethyl acetate, ether, light petroleum, or toluene.

0.2920, made up to 50 c.c. with water, gave  $\alpha - 4.0^\circ$  (Ventzke) in a 2-dcm. tube at  $32^\circ$ , whence  $[\alpha] - 118.8^\circ$ .

The *platinichloride* separates from a fairly concentrated aqueous solution as a bright, ochreous, crystalline powder.

Found: Pt=18.0.

$(C_{10}H_{23}O_4N, HCl)_2PtCl_4$  requires Pt=18.2 per cent.

When kept in a steam-oven for a long time, it slowly swells up and decomposes, forming a dark brown, spongy mass. It darkens at  $188^\circ$  and melts and decomposes at about  $204^\circ$ .

The *aurichloride* was obtained as a greyish-yellow, amorphous precipitate, which decomposed within an hour while remaining in the mother liquor.

The *hydrobromide* crystallises in fine, white needles which melt at  $148-150^\circ$  to a pink liquid:

0.3367 gave 0.1555 AgBr. Br=19.7.

$C_{10}H_{23}O_4N, HBr$  requires Br=19.5 per cent.

It becomes slightly pink after two or three days, and is readily soluble in water, methyl or ethyl alcohol, or glacial acetic acid, sparingly so in acetone, chloroform, or ethyl acetate, and insoluble in amyl alcohol, benzene, carbon disulphide, carbon tetrachloride, ether, light petroleum, or toluene.

0.4209, made up to 50 c.c. with water, gave  $\alpha - 4.4^\circ$  (Ventzke) in a 2-dcm. tube at  $32^\circ$ , whence  $[\alpha] - 90.6^\circ$ .

The *hydriodide* was obtained as a pale brown powder, which melts and decomposes at  $115^\circ$ . The salt, once separated from its aqueous solution, is very sparingly soluble in water, and therefore in the analysis the silver iodide was precipitated from its alcoholic solution:

0.1560 gave 0.8200 AgI. I=28.3.

$C_{10}H_{23}O_4N, HI$  requires I=27.8 per cent.

It is readily soluble in methyl or ethyl alcohols, very sparingly so in water, acetone, chloroform, ethyl acetate, or glacial acetic acid, and insoluble in amyl alcohol, benzene, carbon disulphide, carbon tetrachloride, ether, light petroleum, or toluene.

0.3120, made up to 50 c.c. with alcohol, gave  $\alpha - 2.8^\circ$  (Ventzke) in a 2-dcm. tube at  $32^\circ$ , whence  $[\alpha] - 77.8^\circ$ .

The *sulphate* separated from water in pale pink, radiating plates which, when washed with a mixture of equal parts of absolute alcohol and ether, melted at  $193^\circ$  to a pink liquid, with slight decomposition:

0.5120 gave 0.1794  $\text{BaSO}_4$ .  $S=4.8$ .

$(\text{C}_{19}\text{H}_{23}\text{O}_4\text{N})_2 \cdot \text{H}_2\text{SO}_4$  requires  $S=4.3$  per cent.

It is readily soluble in carbon tetrachloride, chloroform, ethyl alcohol, or toluene, and almost insoluble in acetone, amyl alcohol, benzene, carbon disulphide, ethyl acetate, ether, or light petroleum.

0.5600, made up to 50 c.c. with water, gave  $\alpha=7.2^\circ$  (Ventzke) in a 2-dcm. tube at  $32^\circ$ , whence  $[\alpha] - 111.4^\circ$ .

The *phosphate* did not crystallise from water, but was obtained as a powder, which melted at  $117^\circ$  to a pale brown, transparent liquid:

0.4312 gave 0.1175  $\text{Mg}_2\text{P}_2\text{O}_7$ .  $P=7.6$ .

$\text{C}_{19}\text{H}_{23}\text{O}_4\text{N} \cdot \text{H}_3\text{PO}_4$  requires  $P=7.3$  per cent.

This salt quickly absorbs moisture when left exposed to a damp atmosphere, and becomes viscous. It is readily soluble in water, alcohol, methyl alcohol, or glacial acetic acid, sparingly so in chloroform, ethyl acetate, or ether, and insoluble in acetone, amyl alcohol, benzene, carbon disulphide, carbon tetrachloride, light petroleum, or toluene.

0.5390, made up to 50 c.c. with water, gave  $\alpha=6.1^\circ$  (Ventzke) in a 2-dcm. tube at  $32^\circ$ , whence  $[\alpha] - 98.2^\circ$ .

The *nitrate* crystallises from water in voluminous, fine, feathery tablets melting at  $122^\circ$  to a transparent, pink liquid. An attempt was made to determine the nitric nitrogen by the Crum-Frankland method, but as soon as sulphuric acid was mixed with a solution of 0.1367 gram of the nitrate in the nitrometer, a blood-red coloration was at once produced, and only 1.0 c.c. of moist nitric oxide was evolved at  $35^\circ$  and 750 mm. The percentage of nitric nitrogen thus found is only 0.38, whilst that required for  $\text{C}_{19}\text{H}_{23}\text{O}_4\text{N} \cdot \text{HNO}_3$  is 3.80 per cent. Moreover, duplicate analyses did not always agree, and the nascent nitric acid reacts with the alkaloid before it does with mercury:

0.1965 gave 0.4240  $\text{CO}_2$  and 0.1090  $\text{H}_2\text{O}$ .  $C=58.7$ ;  $H=6.1$ .

$\text{C}_{19}\text{H}_{23}\text{O}_4\text{N} \cdot \text{HNO}_3$  requires  $C=58.2$ ;  $H=6.1$  per cent.

It is readily soluble in water, chloroform, methyl or ethyl alcohol, glacial acetic acid, acetone, or carbon disulphide, sparingly so in benzene, carbon tetrachloride, ethyl acetate, ether, or toluene, and insoluble in amyl alcohol or light petroleum.

0.6835, made up to 50 c.c. with water, gave  $\alpha=9.1^\circ$  (Ventzke) in a 2-dcm. tube at  $32^\circ$ , whence  $[\alpha] - 115.4^\circ$ .

The acetate was obtained as a pale brown, transparent, viscid varnish:

0.2780 gave 0.6610  $\text{CO}_2$  and 0.1920  $\text{H}_2\text{O}$ .  $\text{C}=64.8$ ;  $\text{H}=7.6$ .

$\text{C}_{19}\text{H}_{23}\text{O}_4\text{N}, \text{C}_2\text{H}_4\text{O}_2$  requires  $\text{C}=64.8$ ;  $\text{H}=7.0$  per cent.

It is readily soluble in water, chloroform, methyl or ethyl alcohol, or glacial acetic acid, sparingly so in acetone or ethyl acetate, and insoluble in amyl alcohol, benzene, carbon disulphide, carbon tetrachloride, ether, light petroleum, or toluene.

The *oxalate* crystallises from water in long, pale yellow, prismatic crystals, which darken and melt at  $182^\circ$  with effervescence:

0.1670 gave 0.0492  $\text{CaC}_2\text{O}_4$ .  $\text{C}_2\text{H}_2\text{O}_4=20.72$ .

$\text{C}_{19}\text{H}_{23}\text{O}_4\text{N}, \text{C}_2\text{H}_2\text{O}_4$  requires  $\text{C}_2\text{H}_2\text{O}_4=21.48$  per cent.

It is fairly readily soluble in water, methyl alcohol, or glacial acetic acid, sparingly so in acetone, ether, or ethyl alcohol, and insoluble in amyl alcohol, benzene, carbon disulphide, carbon tetrachloride, chloroform, ethyl acetate, light petroleum, or toluene.

0.9340, made up to 50 c.c. with water, gave  $\alpha-12.3^\circ$  (Ventzke) in a 2-dcm. tube at  $32^\circ$ , whence  $[\alpha] -114.2^\circ$ .

The *citrate* is an amorphous, yellowish-white powder, which melts at  $82-85^\circ$  to a transparent, pale brown liquid:

0.1135 gave 0.2680  $\text{CO}_2$  and 0.0735  $\text{H}_2\text{O}$ .  $\text{C}=64.3$ ;  $\text{H}=7.1$ .

$(\text{C}_{19}\text{H}_{23}\text{O}_4\text{N})_3\text{C}_6\text{H}_6\text{O}_7$  requires  $\text{C}=64.1$ ;  $\text{H}=6.4$  per cent.

It is appreciably hygroscopic, readily soluble in water, methyl or ethyl alcohol, or glacial acetic acid, sparingly so in acetone, amyl alcohol, carbon disulphide, chloroform, or ethyl acetate, and insoluble in benzene, carbon tetrachloride, ether, light petroleum, or toluene.

0.1595, made up to 50 c.c. with water, gave  $\alpha-2.0^\circ$  (Ventzke) in a 2-dcm. tube at  $32^\circ$ , whence  $[\alpha] -108.6^\circ$ .

The *tartrate* is a pink, crystalline powder, which melts at  $116-118^\circ$  to a pale brown, transparent liquid:

0.1080 gave 0.2475  $\text{CO}_2$  and 0.0650  $\text{H}_2\text{O}$ .  $\text{C}=62.5$ ;  $\text{H}=6.6$ .

$(\text{C}_{19}\text{H}_{23}\text{O}_4\text{N})_2\text{C}_4\text{H}_6\text{O}_6$  requires  $\text{C}=62.4$ ;  $\text{H}=6.4$  per cent.

It is somewhat hygroscopic, readily soluble in water, methyl or ethyl alcohol, or glacial acetic acid, sparingly so in amyl alcohol, benzene, carbon disulphide, chloroform, or ethyl acetate, and insoluble in acetone, carbon tetrachloride, ether, light petroleum, or toluene.

0.1635, made up to 50 c.c. with water, gave  $\alpha-1.8^\circ$  (Ventzke) in a 2-dcm. tube at  $32^\circ$ , whence  $[\alpha] -95.5^\circ$ .

The *picrate* is a bright yellow, crystalline powder, which becomes brown at  $171^\circ$  and melts at  $198^\circ$ :

0.1158 gave 0.2258  $\text{CO}_2$  and 0.0510  $\text{H}_2\text{O}$ .  $\text{C}=53.2$ ;  $\text{H}=4.8$ .

$\text{C}_{19}\text{H}_{23}\text{O}_4\text{N}, \text{C}_6\text{H}_3\text{O}_7\text{N}_3$  requires  $\text{C}=53.7$ ;  $\text{H}=4.7$  per cent.

It is a non-deliquescent, crystalline powder, readily soluble in acetone, chloroform, methyl or ethyl alcohol, glacial acetic acid, or ethyl acetate, sparingly so in water, amyl alcohol, benzene, or carbon disulphide, and almost insoluble in carbon tetrachloride, ether, light petroleum, or toluene.

0.2658, made up to 50 c.c. with water, gave  $\alpha - 1.5^\circ$  (Ventzke) in a 2-dem. tube at  $32^\circ$ , whence  $[\alpha] - 49.9^\circ$ .

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### XXXV.—Coagulation of Metal Sulphide Hydrosols. Part I. Influence of Distance between the Particles of a Sol on its Stability. Anomalous Protective Action of Dissolved Hydrogen Sulphide.

By JÑANENDRA NATH MUKHERJEE and NAGENDRA NATH SEN.

THE coagulation of the sulphide sols has been studied by a fairly large number of investigators. There is, however, fundamental disagreement between the results obtained by different authors. It was suggested by one of us in a previous paper (*J. Amer. Chem. Soc.*, 1915, **37**, 2024) that the discrepancy is due to the difference in the methods of observation, some of which are undoubtedly defective. The method used in that paper is a comparative one, and is based on visual observation of the changes in the sol with time. It will be conceded that no objection can be taken against it, although it has one disadvantage in so far as it is not instrumental. This does not in any way interfere with the trend of the results. The method is found to be the most suitable one and gives concordant numbers.

Contrary to the observations of Freundlich (*Zeitsch. physikal. Chem.*, 1903, **44**, 129), it was shown that dilution with pure water increases the stability of arsenious sulphide hydrosols to coagulation by electrolytes. The electrolytes studied were all salts of univalent cations. The difficulty in explaining the observed facts on the basis of the adsorption theory as developed by Freundlich (*loc. cit.*; *ibid.*, 1910, **73**, 385; 1913, **83**, 97; **85**, 398, 641) was mentioned. This point has also received attention from Kruyt and Spek. (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1158), who examined three electrolytes, namely, the chlorides of potassium,

barium, and aluminium, but could not find the stabilising influence of dilution of the sols for ions other than potassium. They do not seem to recognise that the adsorption theory as it stands is insufficient to explain all the facts observed, and do not consider the influence that the distance between the particles of the sol may have on the stability of the sol.

Further, Young and Neal (*J. Physical Chem.*, 1917, **21**, 14), in a thorough study of cupric sulphide hydrosols, remark: "the amount of electrolyte required is independent of the dilution of the sol within wide limits. This latter was found to be true within rather close limits by Freundlich for arsenic sulphide sols." The method used by Young and Neal consists in mixing equal volumes (2 c.c. each) of electrolyte and sol and noting the respective concentration of electrolyte that just produces complete separation of the colloid in twenty-four hours and that which just fails to do so. These two limiting concentrations give a measure of the stability of the sol or the coagulative power of the electrolyte. This method is one due to Freundlich, and generally used by other workers. It will be noted that the concentrations of electrolytes employed are, necessarily, such as would require a fairly long time for the complete separation of the colloid. In the earlier paper (*loc. cit.*), the process of coagulation was discussed in detail, and it was stated that "the time for complete settling is not characteristic of the rate of coagulation." The justification of any method lies in so far as it indicates the progress of coalescence. The increased mass of particles with progress of coalescence introduces a new factor, namely, their gravitational effect, which masks the true behaviour of the sol, as will be clear from the following observations on mercuric sulphide sols.

These sols are opaque unless very dilute. On the addition of electrolytes, there is a quiescent period followed by a sharp clearing of the whole liquid. At this stage, the liquid loses its homogeneous appearance, and visible clots are found suspended throughout the liquid. As the change is sharp, the times noted by different observers agree satisfactorily. In this way, it is found that a mercuric sulphide sol, on saturation with hydrogen sulphide, requires a longer time for the observed change than when it is not so treated—the electrolyte concentration, of course, being identical.

These experiments leave no doubt that dissolved hydrogen sulphide increases the stability of the sol. The subsequent settling of these clots, however, requires a very long time, which is about the same for both samples. So long as the respective times required for the clearing of the sols are very small compared with the time required for the subsequent settling of the clots, it is found that

the times that are necessary for the complete separation of the colloid do not differ much in the two cases. However, with electrolyte concentrations where the clearing requires intervals comparable with that required for the subsequent settling of the clots, regular differences in stability are observed even if the times necessary for complete separation of the colloid are noted.

*Influence of Dilution on the Stability of a Sol.*

The method employed is to mix 5 c.c. each of sol and electrolyte in carefully cleansed test-tubes. For reasons discussed in the previous paper, the electrolyte is always added to the sol. Thorough mixing is secured by pouring the mixed liquids from one test-tube to another and repeating the process. The mixed liquid is shaken regularly at short intervals, and the changes with time are observed. As before, the times required for perceptible change in the sol, for the attainment of maximum opacity, and for the first appearance of visible particles are noted. The time for complete separation of the colloid is also noted when thought desirable. The comparison is always carried out side by side. For sols of mercuric and cupric sulphides, the time for the appearance of visible particles is noted. With dilute sols, it is necessary to note the time for complete settling of the particles.

Experiments were made on arsenious sulphide sols with solutions of hydrogen, ammonium, potassium, lithium, barium and aluminium chlorides, aluminium sulphate, and thorium nitrate. With sols of mercuric and cupric sulphides, solutions of potassium, ammonium and barium chlorides, aluminium sulphate, and thorium nitrate only were studied. All the glass vessels were cleansed by dipping them for twenty-four hours in chromic acid solution after they had been washed with dilute alkali hydroxide. The need for scrupulous care in the washing of the vessels and avoiding dust or other impurities cannot be too strongly emphasised. This holds especially for the extremely dilute solutions used in some cases.

(a) *Arsenious Sulphide Sols.*

In the presence of salts having univalent cations, dilution of the sol increases its stability in each case. The magnitude of the stabilising effect of dilution will be evident from table I. The electrolyte concentrations given are *end* concentrations, that is, what results after mixing. Sols mentioned in the several tables are different unless stated otherwise. "Coagulation" means the

breaking up of the colloid into flakes so that the liquid is clear or very slightly coloured.

TABLE I.

Sol A contained 17.58 millimoles of arsenious sulphide per litre. Sol B was prepared by diluting sol A five times, and sol C by diluting sol A ten times, with pure water.

Electrolyte: lithium chloride.

Dilution (after mixing).	Sol. A.	Sol. B.	Sol. C.
5N/16 ...	—	—	Coagulation after 20 seconds.
5N/32 ...	—	Coagulation after 30 seconds.	Coagulation after 50 minutes.
N/8.....	Instantaneous coagulation.	Coagulation after half an hour.	Perceptible change after 8 minutes. Coagulation after 2½ hours.
N/16 ...	Change perceptible on mixing. Coagulation not observed after 1½ hours.	Change just after mixing not per- ceptible.	Change perceptible after 45 minutes.

On the other hand, in the presence of the salts of aluminium and thorium, the stability decreases on dilution, as will be seen from table II. The data refer to the same three sols. The observations in tables I and II were completed within two days, and neglecting the slight "ageing" during this interval, the data may be taken as comparable.

TABLE II.

Electrolyte: thorium nitrate.

Dilution.	Sol. A.	Sol. B.	Sol. C.
N/10,000	Instantaneous coagulation.	Instantaneous coagulation.	Instantaneous coagulation.
N/20,000	Perceptible turbidity just after mixing. Sol changes slowly.	Coagulation in 2 minutes.	Coagulation within half a minute.
N/30,000	Perceptible turbidity after half an hour.	Perceptible turbidity after 5 minutes.	Coagulation in 4 minutes.
N/40,000	—	—	Coagulation in 53 minutes.

Solutions of salts of bivalent cations display an interesting aspect of the effect of dilution of the sol on its stability. With dilute



sols, the stability increases on dilution, whereas with sols very rich in sulphide content, the stability diminishes on dilution, and for a rich sol it is possible to reach a limit where on further dilution the sol becomes more stable. Moreover, from table III it will be seen that the stability relations on dilution vary with the concentration of the electrolyte itself.

TABLE III.

Electrolyte: barium chloride.

Arsenious sulphide sol containing 19.45 millimoles per litre.

Dilution of Electrolyte.	Original Sol.	Sol diluted 4 times.	Sol diluted 16 times.
N/800 ...	Complete coagulation in 1 minute.	Change perceptible in 20 seconds. Coagulation after 4 minutes.	Perceptible change after 1 minute. Coagulation after 12 minutes.
N/1000 ...	Change perceptible after half a minute. Clots appear throughout after 17 minutes.	Change perceptible in 1 minute. Clots appear throughout after 18 minutes.	Change perceptible after 2 minutes. Clots appear throughout after 26 minutes.
N/1200 ...	Change perceptible in 2 minutes. Clots appear after 1 hour 7 minutes.	Change perceptible in 2 minutes. Clots appear after 52 minutes.	Change perceptible after about 3 minutes. Clots appear after 1 hour 1 minute.

(b) *Mercuric and Cupric Sulphide Sols.*

In the case of mercuric and cupric sulphide sols, it is found that dilution increases the stability of the sol irrespective of the nature of the electrolyte. The effect cannot reasonably escape observation.

All these apparently anomalous facts can be explained on the assumption that distance between the particles of a sol is an important factor in determining its stability. On the adsorption theory of Freundlich, coagulation is due to the neutralisation of the charge of the particles of the sol by adsorbed cations. Other things being equal, it follows that an increase in the total surface of the colloid would mean a decrease in the surface concentration of the cation, so that a higher concentration of the electrolyte would now be necessary to neutralise the charge on the particles. The amount adsorbed is necessarily small, and its effect can only be perceptible when (a) the difference in surface is great compared with the total quantity of the electrolyte present, that is, (b) when the electrolyte concentration is sufficiently low. It is evident that for the concentrations employed in the case of salts of univalent

cations the difference in stability predicted by the adsorption theory on dilution would be negligible. The adsorption theory thus predicts that dilution of the sol will always diminish its stability, and in the limiting case of salts of univalent cations, this theoretical diminution may not be perceptible.

It has been assumed in the above discussion that the individual particles in the sol do not change in any way on dilution, and hence the total surface of the colloidal particles will decrease proportionally to the dilution of the sol.

The observed increase in stability cannot thus be explained by the adsorption theory as it stands. However, if it is considered that dilution also increases the distance between the particles of a sol, it explains easily the increase in stability observed. It may be stated here that Freundlich's adsorption theory does not contemplate any effect of the distance between colloidal particles on the stability of the sol. The increased distance somehow decreases the facility for coalescence, and thus increases its stability, as will be evident from the sequel.

Dilution thus brings into play two factors which have opposite effects on the stability of the sol. The observed increase or decrease in stability is due to the predominating influence of one over the other. The observations given in table III are instructive. In order that the difference in total surface may have a decisive effect on the stability, the quantities withdrawn by adsorption should be comparable with the total quantity of electrolyte present, that is, appreciable differences in the concentrations of the electrolyte in the bulk of the liquid should result with the different dilutions of the sol employed.

As the dilution of the electrolyte increases, the differences in total surface become more dominant in determining the stability of the sol. On the other hand, if the electrolyte concentration is kept constant, then, as the dilution of the sol increases, the total surface of the colloid decreases rapidly, and the effect of adsorption becomes counterbalanced by that of the increase in distance. This is apparent from table IV.

TABLE IV.

Sol contained 19.45 millimoles of arsenious sulphide per litre.  
Electrolyte: aluminium sulphate. Dilution,  $N/4000$ .

Original Sol.	Sol diluted 4 times.	Diluted 16 times.	Diluted 20 times.
Coagulation in 7 minutes.	Coagulates im- mediately on mixing.	Coagulation in 40 seconds.	Coagulation in 50 seconds.

Further dilutions could not be examined, as it became increasingly difficult to follow the changes in the sol.

With mercuric and cupric sulphide sols, much higher concentrations of electrolytes are required for coagulation, and it is interesting to note that in the case of these sols dilution always increases their stability. This may be ascribed to the fact that these sols are generally poorer in colloid content and that the adsorption is much smaller in comparison with the arsenious sulphide sols used.

It should be remarked that the total surface varies directly with the dilution, whereas the mean distance between the particles varies with the cube root of the dilution.

*Comparative Stability of Sols having the same Colloid Content but differing in the Degree of Dispersion.*

In the foregoing, it has been assumed that on dilution the individual particles do not suffer any change. The observations of Coward (*Trans. Faraday Soc.*, 1913, **9**, 142) show that dilution does not bring about a proportionate decrease in the number of sub-microns, and that the migration velocity of the particles in an electric field changes on dilution. Young and Neal (*loc. cit.*) have also observed an increase in migration velocity on dilution with cupric sulphide sols.

In view of these observations, a comparison of a pair of sols which have the same colloid content, but differ in the degree of dispersion, was thought desirable. This is possible with arsenious sulphide sols. Such a comparison has the advantage that, in reality, two sols are compared, one of which has a smaller number of larger particles, whilst the other has a larger number of smaller particles for the same volume. A simple calculation will show that the mean distance between the particles and the total surface of the colloid in a given volume differ in the same ratio. The ratio is given by  $\sqrt[3]{(n_1)} : \sqrt[3]{(n_2)}$ , where " $n_1$ " and " $n_2$ " denote the number of particles present in each case. The relative effects of these factors can thus be compared directly. The finer sol will evidently contain a greater number of particles than the coarser one.

The results leave no doubt as to the greater stabilising effect of increased distance. Of course, here also, with dilute electrolyte solutions and sols differing greatly in the degree of dispersion, the surface effect is perceptible.

By varying the conditions of experiment, a series of sols having the same sulphide content was prepared. For comparison, the coarsest and the finest sols are selected.

TABLE V.

Electrolyte: strontium chloride.

Both sols contained 8.52 millimoles of arsenious sulphide per litre.

Dilution.	Sol I (fine sol).	Sol II (coarse sol).
N/200 .....	Coagulation after a few seconds.	Coagulation after a minute.
N/300 .....	Coagulation after 2 minutes.	Coagulation after 4 minutes.
N/400 .....	Coagulation after 13 minutes.	Turbidity perceptible after 1 minute. A portion of the colloid had separated after 40 minutes.
N/500] .....	The greater portion had separated after 40 minutes.	

It appears that the magnitude of the difference in stability is roughly the same for the different electrolytes. It will be seen from the sequel that dissolved hydrogen sulphide has an anomalous effect on the rate of coagulation of arsenious sulphide sol in the case of certain salts. Here, also, the greater stability of the coarser sol is quite marked. In table VI are given the respective concentrations of an electrolyte which corresponds with about the same coagulation time for these two sols.

TABLE VI.

Electrolyte.	Comparable concentrations.		Remark.
	Sol I.	Sol II.	
SrCl <sub>2</sub> .....	N/500	N/400	In presence of H <sub>2</sub> S.
" .....	N/400	N/300	
LiCl .....	N/8	5N/32	
NH <sub>4</sub> Cl .....	N/20	N/16	
KCl .....	N/20	N/16	

*Influence of Dissolved Hydrogen Sulphide on the Stability of Metal Sulphide Sols.*

*(a) Arsenious Sulphide.*

In the paper referred to, it was stated that dissolved hydrogen sulphide stabilises arsenious sulphide sols against coagulation by electrolytes. The electrolytes used at that time were salts of univalent cations. It has subsequently been observed that arsenious sulphide sols behave in an anomalous manner. When solutions of

barium and strontium chlorides, magnesium sulphate, and thorium nitrate are used, the sol containing hydrogen sulphide becomes less stable. Tables VII and VIII show that the diminution in stability is as marked as the increase in stability observed with the other electrolytes. In each set of experiments, the sol and the electrolyte were both saturated with hydrogen sulphide freed from impurities. Five c.c. of each were withdrawn by means of a pipette with the help of a rubber hand pump and kept in separate test-tubes. The liquids were then mixed as usual and kept well corked with india-rubber stoppers. Care should be taken that the liquids do not touch the rubber.

TABLE VII.

Arsenious sulphide sol containing 17.58 millimoles per litre.  
Electrolyte: aluminium sulphate.

Dilution.	H <sub>2</sub> S absent.	H <sub>2</sub> S present.
N/24,000 ...	Complete coagulation after 2 minutes.	Partial coagulation after 3½ minutes.
N/30,000 ...	Partial coagulation after 6 minutes. Complete after 11 minutes.	Only slight turbidity after 21 minutes.

TABLE VIII.

*Comparable Concentrations.*

Electrolyte.	Sol I.		Sol II.		Sol III.	
	H <sub>2</sub> S absent.	H <sub>2</sub> S present.	H <sub>2</sub> S absent.	H <sub>2</sub> S present.	H <sub>2</sub> S absent.	H <sub>2</sub> S present.
KCl .....	N/18	N/8	—	—	N/16	N/8
NH <sub>4</sub> Cl .....	N/20	N/12	N/20	N/12	N/20	N/12
BaCl <sub>2</sub> .....	N/800	N/1000	N/800	N/1000	—	—
SrCl <sub>2</sub> .....	N/300	N/400	N/300	N/400	—	—
Th(NO <sub>3</sub> ) <sub>4</sub> .....	N/10,000	N/12,000	—	—	—	—

The data with thorium nitrate refer to the sol mentioned in table VII. Sols I and II are the same as those in tables V and VI. Sol III is a fine sol containing 34.8 millimoles of arsenious sulphide per litre.

The results show that the magnitude of the stabilising effect varies somewhat with the quality of the sol used. A quantitative comparison is beyond the scope of the present paper.

(b) *Mercuric Sulphide.*

Hydrogen sulphide has a similar influence on mercuric sulphide sols. Increase in stability was observed for ammonium and

potassium chlorides and a diminution for barium and strontium chlorides.

The sols were prepared as usual from the freshly precipitated hydroxide or sulphide after they had been washed free from electrolytes. The sols had a blackish-grey appearance.

The coagulation of these sols differs in one respect from that of arsenious sulphide sols, possibly due to the fact that they are comparatively poorer in sulphide content. Sols, unless very rich in sulphide, show a minimum coagulation time (as defined here); for example, a mercuric sulphide sol gave a clearance time of about two minutes from  $N/20$ - to  $N/300$ -barium chloride. With more dilute solutions, the coagulation time increased rapidly as usual.

### (c) Cupric Sulphide.

It is well known that dissolved hydrogen sulphide markedly stabilises the pure sulphide sols both in aqueous and non-aqueous media (Lottermoser, *J. pr. Chem.*, 1907, [ii], 75, 293) and facilitates their solution. It is natural to conclude that the same protective effect would be observed with the sulphides of different metals in the presence of electrolytes. This is, however, not the case here. It has been found that hydrogen sulphide diminishes the stability of cupric sulphide sols. This holds good for all the electrolytes studied, namely, potassium, ammonium, strontium, and barium chlorides, and aluminium sulphate, and the anomaly observed with arsenious and mercuric sulphide sols is absent. Young and Neal (*loc. cit.*) could not find any perceptible effect of hydrogen sulphide on the stability. This is probably due to the method they used.

The observed diminution in stability can be understood from an observation of Young and Neal. They find that hydrogen sulphide diminishes the velocity of migration of the particles of a cupric sulphide sol in an electric field. It follows from the well-known Helmholtz-Lamb formula (*Rep. Brit. Assoc.*, 1887, 495) that a diminution of the electric charge of the particles takes place provided that other factors remain constant. The result will be a diminution in stability, as a smaller amount of adsorbed cations will now be required to discharge the particles. As it is not clear that simultaneous measurements of viscosity and other properties were made, the parallelism loses much of its significance.

Solutions of ammonium, potassium, barium, and strontium chlorides, and aluminium sulphate were studied. With ammonium and potassium chlorides, nearly saturated solutions have to be used.

TABLE IX.

Electrolyte.	Dilution.	Clearance time.	
		H <sub>2</sub> S absent.	H <sub>2</sub> S present.
KCl .....	—	6 minutes.	A few seconds.
BaCl <sub>2</sub> .....	N/20	9    "	4 minutes.
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....	N/2000	13   "	9    "

*Protective Action of Alkali Sulphides and Alkali Hydroxides.*

Solutions of potassium and sodium sulphides have a more marked protective action. This stabilising influence has been found for ammonium, potassium, barium, and strontium chlorides, and aluminium sulphate on hydrosols of cupric, mercuric, and arsenious sulphides. The behaviour of the sols is thus very regular.

This is also the case with alkali hydroxides. A trace greatly facilitates the preparation of sols rich in sulphide, and largely increases their stability. The protective action of alkali sulphides is probably due to the free alkali hydroxide present as a result of hydrolysis.

Since these substances dissolve arsenious sulphide with the formation of arsenites and thioarsenites, it is not possible in this case to refer the protective action observed to the hydroxidions alone. Indeed, the liquid obtained by dissolving in a few c.c. of dilute alkali hydroxide as much arsenious sulphide as possible has an equally marked protective action on the sols of these three sulphides. However, as alkali hydroxide does not react with the other sulphides and produces similar protective action, it is probably that the effect of all these substances is due to the trace of free alkali hydroxide present as the result of hydrolysis.

Freundlich (*Zeitsch. physikal. Chem.*, 1903, **44**, 144) has observed that salts of alkali metals with organic anions of large mass have a lower coagulating power than the corresponding salts of inorganic acids. He refers this to the protective action of these anions, due to greater adsorbability, but in view of the preceding this can as well be due to the trace of alkali hydroxide present on hydrolysis.

In conclusion, it may be stated that the anomalous influence of hydrogen sulphide is not without parallel. Recently Freundlich has found somewhat similar behaviour with ferric hydroxide hydrosol (*Biochem. Zeitsch.*, 1917, **81**, 87). An actual reversion of stability was not, however, observed in this case. So far as can be understood from the abstract of the paper, he explains these irregularities as due to selective adsorption (*loc. cit.*). It remains

to be seen how far these observations can be explained on the basis of the existing theories.

Our best thanks are due to Sir P. C. Rây and to Dr. J. C. Ghosh.

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### XXXVI.—*A Simple Form of Apparatus for Estimating the Oxygen Content of Air from the Upper Atmosphere.*

By FRANCIS WILLIAM ASTON.

FROM meteorological considerations, it is probable that air in the stratosphere or isothermal layer is stagnant, hence, owing to their different densities, the relative percentage of oxygen and nitrogen will not be identical with that in the troposphere, where mixing is practically perfect. It is therefore of great importance that exact analyses should be made whenever possible of samples of air brought down from the great altitudes now available to aeroplanes in order to find out at what height such gravitational separation becomes evident to chemical analysis. For this purpose, it is enough to determine the oxygen content of the sample after this has been dried and freed from carbon dioxide.

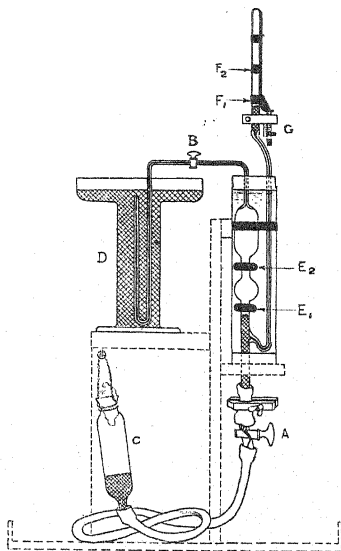
A complete and exceedingly accurate method for determining the percentage of oxygen in air volumetrically has been described by Watson (T., 1911, 99, 1460). The apparatus which forms the subject of this paper is a modification of this, in which, by measuring the difference only in oxygen content between the sample and normal air, very considerable simplifications may be made, the pump and the cathetometer being rendered unnecessary.

The samples are contained in test-tubes holding rather more than is required for an analysis (10 c.c.), in the tops of which have been fused a little potassium hydroxide. Here they remain over mercury for at least two hours before analysis in order to remove carbon dioxide and water vapour.

The measuring burette and barometer tube (see figure) are normally kept full of mercury with the stopcock *A* turned on to avoid fracture by expansion. In order to perform an analysis, the capillary stopcock *B* is closed and the reservoir *C* lowered until the level of the mercury in the barometer tube is a little below its



upper and broader part. The stopcock *A* is then closed, and the sample tube held down over the inverted syphon tube in the mercury trough *D*. When the capillary stopcock *B* is now opened, the air flows into the upper part of the burette and the mercury rises again to the top of the barometer tube; in order to prevent this happening with destructive violence, the lower part of the barometer is made of capillary bore (less than 2 mm.). After waiting for a few moments for pressure and temperature to adjust



themselves, the sample tube is raised, flooding the end of the inverted syphon with mercury, the stopcock *A* is opened again, and by lowering the reservoir mercury is caused to flow through the syphon and fill the capillary tube when *B* is turned off.

It will be seen that the volume of air introduced in this way is constant, being the volume of the upper part of the barometer tube (in the actual apparatus a little less than 10 c.c.); the pressure being atmospheric plus the small difference of level between the

top of the syphon tube and the mercury in the trough, the quantity will also be approximately constant. This quantity is now accurately measured by adjusting the mercury level in the burette exactly to the lower fixed reading point,  $E_1$ ; this can be done with the greatest nicety by bringing the mercury nearly up to the mark by manipulation of the reservoir and stopcock, and, finally (with the latter closed), squeezing the short length of rubber pressure-tubing with the screw clip provided as indicated. The volumes of the burette and barometer are such that the surface of the mercury in the latter will be somewhat as indicated in the diagram, and the lower movable reading point,  $F_1$ , may be exactly adjusted to it by means of the micrometer screw,  $G$ .

The barometer and the parts of the burette where readings are taken are all made of the same piece of glass tube 0.9 cm. in internal diameter to eliminate meniscus error. The reading points are all sleeves of brass tube 1 cm. long fitting the glass tubes, clamped in the case of the fixed points, sliding loosely in the case of the moving ones.

The reading of the micrometer having been taken, the air is now forced into the laboratory tube. This is a quartz test-tube holding rather more than 10 c.c., to the top of which (not quite in the centre) has been fused a pellet of phosphorus. These pellets may be easily made by allowing melted phosphorus to flow from a pipette with a narrow mouth into a tall cylinder of cold water. One spherule of about 2—3 mm. in diameter should be ample, and this is introduced into the inverted quartz tube full of mercury, shaken into position, and fused into the side with a touch from a Bunsen flame. When all the air has been transferred from the burette to the quartz tube, the phosphorus is inflamed and then heated to boiling point in order to ensure the complete removal of all oxygen. Some time is allowed for the phosphoric oxide to settle, when the deoxidised air is drawn back into the burette. It was feared when the apparatus was designed that to perform this operation satisfactorily might be difficult, or even impossible, as small bubbles of air were expected to remain behind on the walls of the quartz tube, now of necessity contaminated with the products of combustion. Such bubbles are formed, but they can be dislodged by touching with the syphon tube and then washed with a little mercury into the burette.

In Watson's apparatus, the deoxidised residue was measured at the same volume as the original air, necessitating the determination of two widely different pressures. In the present one, the residue is measured at such a volume that if the air is normal the two pressures measured would be identical, so that a very small differ-

ence of pressure only need be determined. For this purpose, the upper fixed reading point,  $E_2$ , is used, this being set once for all during the construction of the burette, so that the upper part of the burette holds exactly 79.0 per cent. of the whole. The upper movable reading point,  $F_2$ , is also soldered to the sliding carrier at exactly the same height above the lower one as that between the fixed points. Hence it will be seen at once that for normal air the mercury at the measurement of the residue should stand at the upper movable reading point, or, if the dimensions of the apparatus are not quite correct, at a constant small distance above or below it, a correction easily determined at any time by an analysis of normal air. If, on the other hand, there is reduction in the percentage of oxygen present, the mercury will stand at a higher level, the difference being measured on the micrometer.

A decrease of oxygen from 21 per cent. to 20 per cent. corresponds with a change in height of mercury in the ratio of 79 to 80; as the normal difference between the fixed and movable reading points in the apparatus in use is 237 mm., this gives exactly 3 mm. per 1 per cent. change. The micrometer has a range of 10 mm., which is more than ample for the changes expected, and analysis should be consistent to well within one-tenth per cent. on total air, the head of the micrometer being divided in twentieths of a millimetre, corresponding with one-sixtieth per cent.

Temperature errors are minimised by the immersion of the burette and the most of the length of the barometer tube in a small water-jacket. As the time occupied in an analysis is only a few minutes, they are not likely to be serious.

The following readings of the micrometer in mm. obtained with the apparatus will serve as an example. The first set of three were obtained with pure air, which is regarded as containing 21.00 per cent. oxygen, the second with an artificial sample in which the oxygen content had been reduced, by the addition of a known quantity of deoxygenated air, to 20.42 per cent.:

	Pure air.			Sample.		
$F_1$ .....	3.65	3.38	4.83	4.52	5.55	5.40
$F_2$ .....	3.39	3.20	4.55	6.09	7.21	7.06
Diff. ....	0.26	0.18	0.28	1.57	1.66	1.54
Mean diff. ....	0.24			1.59		

Decrease in percentage of oxygen  $\frac{1.59 + 0.24}{3} = 0.61$  giving percentage of oxygen in sample = 20.39, in good agreement with the value expected.

### XXXVII.—*The Resolution of Hyoscine and its Components, Tropic Acid and Oscine.*

By HAROLD KING.

HYOSCINE or scopolamine, the tropyl ester of oscine, and one of the group of Solanaceous alkaloids, receives varied and extensive use in medicine, and has on that account attracted the attention of many workers both from the chemical aspect and from the medicinal.

During the last few years, the subject has acquired an additional interest and importance as a result of the recognition that oscine (or scopoline), the basic hydrolytic product, is capable of resolution into its constituents *d*- and *l*-oscine. This follows from the resolution of benzoyloscine by Tutin in 1910 (T., 97, 1793) and from the partial elucidation of the structural formula of oscine by Schmidt and Hess and their co-workers, whereby it seems certain that oscine, unlike tropine, is not internally compensated. Apart from these two separate results, and in spite of the vast amount of work that has been carried out on oscine and hyoscine, there was nothing known which definitely pointed to this conclusion. Since tropic acid is also capable of resolution, and Gadamer (*Arch. Pharm.*, 1901, 239, 294) has shown that *l*-tropic acid may be obtained by hydrolysis of *l*-hyoscine, it follows that tropyloscine (hyoscine) might exist in ten, or possibly eleven, stereoisomeric forms consisting of four optically active, four partially racemic, two fully racemic, and one double racemic compound. The problem is in some ways analogous to that presented by the ten tetrahydroquinaldinomethylenecamphors obtained by Pope and Read (T., 1913, 103, 1515), but with this difference, that in the case of the hyoscines an approach is at present (apart from the rarity of the materials) not possible from the synthetic side, as hyoscine has as yet not been obtained by the esterification of oscine by tropic acid. The elucidation of the chemistry of the isomeric hyoscines and the correct allocation of the medicinal properties to be attributed to each is of considerable moment for both sciences.

Our knowledge of the hyoscines as revealed by previous workers, so far as it appertains to the present subject, may be very briefly summarised.

Naturally occurring *laevo*-hyoscine has been obtained in a state of purity by several workers, and in the form of its well-crystallised hydrobromide is a commercial product. In the plant, it is apparently accompanied to some extent by *dl*-hyoscine, from which

it can be separated by fractional crystallisation of the hydrobromides. Racemic hyoscine base, which can also be obtained from *l*-hyoscine by the action of alkalis, forms two hydrates, one crystallising with two molecules of water, and known as atrosine (Hesse), the other with one molecule of water. Two attempts to resolve racemic hyoscine are recorded, the first by Schmidt (*Arch. Pharm.*, 1898, **236**, 56), who found that the salt with thiocyanic acid did not separate into two mechanically separable crystalline enantiomorphs, as was the case with racemic lupanine (Schmidt and Davis, *Arch. Pharm.*, 1897, **235**, 196), the second by Gadamer (*Arch. Pharm.*, 1901, **239**, 294), who states that the quinic acid and *d*-mandelic acid salts of *dl*-hyoscine are very readily soluble and possess little crystallising power, and are therefore not suitable for the resolution of hyoscine.

The primary mode of attack adopted in the present investigation is based on some unpublished preliminary experiments by Tutin, who showed that *l*-hyoscine of commerce forms a soluble, deliquescent salt with *d*-bromocamphorsulphonic acid which can be recrystallised from dry ethyl acetate containing alcohol, and also that when *l*-hyoscine is racemised by alkali, the product as a salt with the same acid can likewise be recrystallised, and the successive fractions of salt so obtained show a progressive variation in rotatory power. The author here gratefully acknowledges his indebtedness to Mr. Tutin for placing these results at his disposal.

A quantity of crystalline hydrobromides of feeble levorotatory power, obtained as a by-product in the manufacture of the therapeutically valuable *l*-hyoscine, was fractionally crystallised as a salt with *d*- $\alpha$ -bromo- $\pi$ -camphorsulphonic acid, when the first salt to be isolated was *meteloidine bromocamphorsulphonate* (m. p. 224—227°). This salt crystallises exceedingly well, and contains *i*-meteloidine (compare Pyman and Reynolds, T., 1908, **93**, 2077). On continuing the fractionation, *d*-hyoscine bromocamphorsulphonate was obtained in a state of purity. It melted at 159—160°, and crystallised in glistening, acicular needles.

*d*-Hyoscine hydrobromide was prepared from it, and found to crystallise with three molecules of water and to possess a specific rotatory power  $[\alpha]_D +23.1^\circ$ , which corresponds with a value  $[\alpha]_D +33.4^\circ$  for the *d*-hyoscinium ion. For comparison, some of the maximum values recorded by previous observers for the *laevo*-salt are tabulated below.

*l-Hyosine Hydrobromide.*

	$[\alpha]_D$ , anhydrous salt.	$[\alpha]_D$ , ionic value.
Schmidt <sup>1</sup> .....	-25.7°	-32.5°
Hesse <sup>2</sup> .....	-25.9	-32.7
Thoms and Wentzel <sup>3</sup> .....	-25.76	-32.5
Carr and Reynolds <sup>4</sup> .....	-26.0	-32.8
Willstätter and Hug <sup>5</sup> .....	-26.0	-32.8
King <sup>6</sup> .....	-25.9	-32.7

*d-Hyosine Hydrobromide.*

King <sup>7</sup> .....	+26.3°	+33.2°
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<sup>1</sup> *Arch. Pharm.*, 1892, **230**, 207.    <sup>2</sup> *J. pr. Chem.*, 1901, [iii], **64**, 353.

<sup>3</sup> *Ber.*, 1901, **34**, 1023.

<sup>4</sup> *T.*, 1910, **97**, 1330.

<sup>5</sup> *Zeitsch. physiol. Chem.*, 1912, **79**, 146.

<sup>6</sup> *P.* 504.

<sup>7</sup> *P.* 503.

These values show that the purified *l*-hyosine hydrobromide of previous workers and the *d*-hyosine hydrobromide now isolated for the first time represent one pair out of the eleven possible stereoisomeric hyoscines.

On mixing equal weights of pure *d*- and *l*-hyosine hydrobromides and recrystallising the mixture from water, *dl*-hyosine hydrobromide, also crystallising with three molecules of water and in a form indistinguishable from the active components, was obtained. It differs from the active components in that it very readily effloresces and in that the base obtained from it is crystalline and contains two molecules of water. For the further characterisation of these three related compounds, their *aurichlorides*, *auribromides*, and *picrates* were prepared. The results are shown in the following table:

	<i>l</i> -Hyosine.	<i>d</i> -Hyosine.	<i>dl</i> -Hyosine.
<i>Base—</i>			
Appearance .....	Syrup.	Syrup.	Prism.
H <sub>2</sub> O .....	—	—	2H <sub>2</sub> O
M. p. ....	—	—	38—40°
<i>Hydrobromide—</i>			
Appearance .....	Large rhombic tablets.	Large rhombic tablets.	Large rhombic tablets.
H <sub>2</sub> O .....	3H <sub>2</sub> O	3H <sub>2</sub> O	3H <sub>2</sub> O
M. p. (anhydrous)	193—194°	193—194°	181—182°
$[\alpha]_D$ (anhydrous)	-25.9°	+26.3°	—
<i>Picrate—</i>			
Appearance .....	Slender matted needles.	Slender matted needles.	Needles.
M. p. ....	187—188°	187—188°	173.5—174.5°

	<i>l</i> -Hyoscine.	<i>d</i> -Hyoscine.	<i>dl</i> -Hyoscine.
<i>Aurichloride</i> —			
Appearance .....	Needles, both edges serrated.	Needles, both edges serrated.	Needles, one edge serrated.
M. p. ....	204—205°	204—205°	214—215°
<i>Auribromide</i> —			
Appearance .....	Chocolate-red leaflets.	—	Chocolate-red leaflets.
M. p. ....	187—188°	—	209—210°

Some of these call for further remark in view of the results of previous observers. The racemic base crystallising with  $2\text{H}_2\text{O}$  is probably a purer form of Hesse's atrosine (*Ber.*, 1896, **29**, 1776), which melted at 36—37°, and was obtained by fractionally crystallising commercial samples of hyoscine hydrobromide. It was obtained on one other occasion by Gadamer (*Arch. Pharm.*, 1898, **236**, 382), who gives the melting point 37—38°. The *dl*-hyoscine hydrobromide agrees in its properties with those recorded by Hesse (*Annalen*, 1899, **309**, 75; *J. pr. Chem.*, 1901, [ii], **64**, 353).

The picrates have been recommended for identifying the mydriatic alkaloids by Carr and Reynolds (*T.*, 1912, **101**, 949), who describe *l*-hyoscine and *dl*-hyoscine picrates as slender, matted needles melting respectively at 180—181° and 193°. Neither of these melting points is in agreement with the results here recorded, which, however, do find support in the only two other recorded melting points of the picrates: Schmidt (*Arch. Pharm.*, 1894, **232**, 409) describes *l*-hyoscine picrate as melting at 187—188°, and Finnemore and Braithwaite (*Pharm. J.*, 1912, **89**, 136), from an examination of commercial samples of hyoscine hydrobromide of varying rotatory power, give figures which show that *l*-hyoscine picrate melts at 187—188° and *dl*-hyoscine picrate at 174—175°.

The aurichlorides have been described by almost all previous workers on the hyoscines, but there is complete disagreement between the recorded melting points. This is all the more surprising, as several workers have had in hand pure *l*-hyoscine hydrobromide. To quote only two of these, Schmidt (*Arch. Pharm.*, 1910, **248**, 641) states that *l*-hyoscine aurichloride of various origins has previously been shown to melt when quite pure at 210—214°, whereas Hesse (*J. pr. Chem.*, 1901, [ii], **64**, 274) states that after many crystallisations he never found any salt to melt above 198°. The melting points now recorded for the *d*- and *l*-hyoscine aurichlorides are for salts prepared in two different ways and recrystallised to constant melting point. In substantial agreement with these values, Thoms and Wentzel (*Ber.*, 1901, **34**, 1023) give 204°, and Finnemore and Braithwaite (*loc. cit.*) record

several almost pure commercial *l*-hyosine hydrobromides as furnishing aurichlorides melting at 200—204°.

*Tropic Acid. The Acid Constituent of Hyosine.*

As has already been stated, Gadamer showed that *l*-hyosine on hydrolysis with the base tropine gave *l*-tropic acid. This crude acid, on purification by recrystallisation from water, gave *l*-tropic acid melting at 125—126°, and having a specific rotatory power in water  $[\alpha]_D -71.8^\circ$ . Gadamer regarded this as optically pure, since Ladenburg and Hundt (*Ber.*, 1889, **22**, 2591) record the value  $[\alpha]_D +71.4^\circ$  for pure *d*-tropic acid melting at 127—128°.

Instead of employing a base for the hydrolysis, *l*-hyosine has now been hydrolysed by boiling with dilute hydrochloric acid, when a crude *l*-tropic acid (m. p. 125—127°,  $[\alpha]_D -70.5^\circ$ ) was obtained, which on recrystallisation gave *l*-tropic acid melting at 127—128° and having  $[\alpha]_D -76^\circ$  in water. As this rotation was numerically considerably greater than the value recorded by the aforementioned workers, it was necessary to repeat the resolution of tropic acid.

A comparison of the results obtained with those of previous investigators is shown in the following table:

	Ladenburg and Hundt.	Amenomiya. <sup>1</sup>	King.
<i>Quinine d-tropate</i> —			
M. p. ....	186—187°	189—190°	191.5—192.5°
$[\alpha]_D$ 95 per cent. alcohol .....	—	—	—114°
<i>Quinine l-tropate</i> —			
M. p. ....	178°	184—185°	185—186°
$[\alpha]_D$ 95 per cent. alcohol .....	—	—	—141°
<i>d-Tropic acid</i> —			
M. p. ....	127—128°	126—127°	128—129°
$[\alpha]_D$ water .....	—	—	+81.6°
$[\alpha]_D$ alcohol .....	+71.4°	+71.3°	+71.8°
<i>l-Tropic acid</i> —			
M. p. ....	123°	126°	128—129°
$[\alpha]_D$ water .....	—	—73.7°	—81.2°
$[\alpha]_D$ alcohol ...	—65.1°	—	—

<sup>1</sup> *Arch. Pharm.*, 1902, **240**, 501.

It is at once seen that Ladenburg and Hundt's value  $[\alpha]_D +71.4^\circ$  is the value in alcoholic solution, Gadamer having regarded it as the value in water, as the aforementioned investigators were not



very explicit, merely stating that the specific rotatory power was  $+71.4^\circ$  in solutions of various concentration.

As previous workers appeared to have experienced some difficulty in obtaining pure quinine *l*-tropate from the mother liquors, a variant was made by converting the recovered partly resolved *l*-tropic acid into the quinidine salt. Further, by use of the two stereoisomeric alkaloids quinine and quinidine, but commencing the resolution with quinidine, 55 per cent. of pure quinidine *l*-tropate was first isolated, then an 80 per cent. yield of pure quinine *d*-tropate, and simultaneously a 14 per cent. yield of pure quinine *l*-tropate. On reverting to quinidine, a further 19 per cent. yield of quinidine *l*-tropate was obtained. In this way, approximately 84 per cent. of the tropic acid was resolved into its constituents. It would, however, be probably an advantage, other factors being equal, to start the resolution with quinine and follow with quinidine, since experiment showed that, starting with quinine, 66 per cent. of quinine *d*-tropate was obtained pure, and, as stated above, starting with quinidine only, 55 per cent. of quinidine *l*-tropate could be separated.

It is interesting to note that previous attempts to use quinine and quinidine for the resolution of externally compensated acids, in the above sense, have not always been successful. Whereas Fischer, Scheibler, and Groh (*Ber.*, 1910, **43**, 2022) found that in the resolution of formyl- $\beta$ -alanine, quinine separated the *l*-component and quinidine the *d*-component, Scheibler and Wheeler (*Ber.*, 1911, **44**, 2686) found that in the resolution of *dl*-leucine the same two alkaloids always gave the *l*-acid first. This was also the experience of McKenzie (*T.*, 1899, **75**, 969) in the resolution of mandelic acid.

#### *Oscine. The Basic Hydrolytic Product of Hyoscine.*

There are numerous instances recorded in the literature of the hydrolysis of *l*-hyoscine by alkalis, but the basic hydrolytic product, oscine,  $C_8H_{13}O_2N$ , was invariably found to be devoid of optical activity, even in the presence of borates or strong acids (Gadamer, *Arch. Pharm.*, 1901, **289**, 322). The only occasion on which *l*-hyoscine has been hydrolysed by acids is recorded by Hesse (*Annalen*, 1892, **271**, 100), who carried out the hydrolysis with concentrated hydrochloric acid in a sealed tube at  $80-100^\circ$ . This furnished the base, oscine, but there is no record of its polarimetric examination.

To decide this matter, pure *l*-hyoscine has now been hydrolysed by boiling with excess of 10 per cent. hydrobromic acid, the change

of rotation being followed polarimetrically. When hydrolysis was complete, the *l*-tropic acid was removed by extraction with ether, and the residual solution of oscine hydrobromide was found to be devoid of optical activity. As Tutin had shown that benzoyl-*d*-oscine on hydrolysis with hydrochloric acid gave *d*-oscine, the hydrolysis of *l*-hyoscyne was repeated, using hydrochloric acid. Again the oscine hydrochloride solution was inactive. As it was conceivable that the benzoylation of oscine might have effected some fundamental change in the configuration of oscine, whereby the benzoylated product became externally compensated, and therefore capable of resolution, it was necessary to prove that oscine itself could be resolved into its constituents, *d*- and *l*-oscine.

Several salts of oscine with optically active acids were prepared and examined. The salt with Reychler's camphorsulphonic acid was not obtained crystalline, but with *d*- $\alpha$ -bromo- $\pi$ -camphorsulphonic acid a markedly crystalline salt was obtained, which melted at 232–233°. This salt, however, proved to be a partial racemate. With *d*- $\alpha$ -bromo- $\beta$ -camphorsulphonic acid, a very readily soluble, crystalline salt was isolated, but beyond recording a single rotation, it was not followed further, as *d*-tartaric acid was found to be eminently suitable for the resolution of oscine.

The separation of *dl*-oscine into its two pure enantiomorphs can be effected by use of *d*-tartaric acid alone, the acid salts being used for this purpose in aqueous solution. The more sparingly soluble salt, which separated almost pure after two crystallisations, is *l*-oscine *d*-hydrogen tartrate monohydrate (m. p. 173–174°, anhydrous), which crystallises magnificently in clear tablets or octahedra. Employing 14 grams of oscine in combination with a like quantity of *d*-tartaric acid, between 70 and 80 per cent. of this component was separated with no great difficulty. The *d*-oscine *d*-hydrogen tartrate contained in the mother liquors can be obtained pure either by isolation as the monohydrate, a very readily soluble, metastable salt melting below 100°, or, preferably, as the stable anhydrous salt (m. p. 167–168°). The proportion of this salt obtained in a state of purity is largely a function of time, as it crystallises very slowly, but uncommonly well, in hexagonal-shaped tablets from the cold, syrupy mother liquors.

*l*-Oscine picrate, hydrochloride, and base were obtained without bringing into contact with alkali at any stage, but this was found afterwards to be an unnecessary precaution, as *l*-oscine is not racemised by boiling with 10 per cent. acid or alkali, and only partly by saturated baryta at 150°.

*d*-Oscine picrate, hydrochloride, and base were prepared in the usual manner by liberating the base from the hydrogen tartrate

by a strong alkali. The properties of these salts as compared with the *dl*-oscine salts are shown in the following table:

<i>Base</i> —	<i>d</i> -Oscine.	<i>l</i> -Oscine.	<i>dl</i> -Oscine.
Appearance .....	Needles.	Needles.	Needles or tablets.
M. p. ....	109—110°	109—110°	109—110°
$[\alpha]_D$ water .....	+54.8°	—52.4°	—
<i>Picrate</i> —			
Appearance .....	Dimorphous rhombs and needles.	Dimorphous rhombs and needles.	Flattened rhombs.
M. p. ....	237—238°	237—238°	237—238°
<i>Hydrochloride</i> —			
Appearance .....	Warts composed of prisms. Very deliquescent.	Warts composed of prisms. Very deliquescent.	Warts composed of prisms (anhydrous). Tablets (hydrated).
M. p. ....	273—274°	273—274°	273—274°
$[\alpha]_D$ in water of basic ion .....	+24.0°	—24.2°	—

It is noteworthy that the active and *dl*-isomerides have the same melting points, and mixtures of the active with the *dl* show no depression of the melting point. In the case of the bases, the melting-point curve is thus of the same type as is found for the camphoroximes.

By hydrolysis of benzoyl-*d*-oscine, Tutin (*loc. cit.*) obtained a value for the *d*-oscinium ion of  $[\alpha]_D + 129^\circ$ ,\* which he regarded as only approximate. As this was very different from the value recorded above, it was necessary to repeat the resolution of benzoyl-oscine. Pure benzoyl-*d*-oscine hydrochloride was obtained having a value  $[\alpha]_D + 13.4^\circ$  for the benzoyl-*d*-oscinium ion, in agreement with the value  $+12.9^\circ$  calculated from the rotation of the bromo-camphorsulphonate. This hydrochloride was submitted to hydrolysis by acids and alkalis. In both cases the result was the same, a solution being obtained which, on removal of benzoic acid, gave values  $[\alpha]_D + 26.0^\circ$  and  $[\alpha]_D + 25.8^\circ$ , by acid and alkali hydrolysis respectively, for the *d*-oscinium ion. Moreover, the hydrochloride and picrate were isolated from the product of acid hydrolysis, and the properties were in agreement with the *d*-oscine salts obtained by the tartaric acid resolution of oscine.

#### *Interpretation of Results.*

The question now arises, which of the eight possible optically active stereoisomeric hyoscines do *d*- and *l*-hyoscine represent?

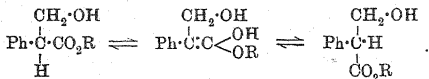
\* Tutin gives the value  $+77.7^\circ$ , having overlooked the loss of the benzoyl group.

The various possibilities are shown in the following table, the centre column representing optically pure forms, which, combined, as shown by the arrows, yield partially racemic forms:

Partial racemates.	Optically pure forms.	Partial racemates.
5. <i>dl</i> -troyl- <i>d</i> -oscine	1. <i>l</i> -troyl- <i>d</i> -oscine	7. <i>l</i> -troyl- <i>dl</i> -oscine
	2. <i>l</i> -troyl- <i>l</i> -oscine	
6. <i>dl</i> -troyl- <i>l</i> -oscine	3. <i>d</i> -troyl- <i>d</i> -oscine	8. <i>d</i> -troyl- <i>dl</i> -oscine
	4. <i>d</i> -troyl- <i>l</i> -oscine	

Of these, 1 to 6 are at once excluded, since *l*-hyoscyne on hydrolysis with acid or alkali gives *l*-tropic acid and *dl*-oscine, whereas benzoyl *d*-oscine under similar conditions yields optically pure *d*-oscine. On these grounds, *l*- and *d*-hyoscyne, represented by 7 and 8, are therefore partially racemic esters, *l*-hyoscyne being a molecular combination of *l*-troyl-*d*-oscine and *l*-troyl-*l*-oscine, whilst *d*-hyoscyne is a similar combination of *d*-troyl-*d*-oscine and *d*-troyl-*l*-oscine.

The known inactivation of *l*-hyoscyne by alkalis would, on this basis, simply consist in the change of configuration of the troyl portion of the molecule, probably through the intermediary of the



enolic form, and each constituent ester of the partial racemate should give rise to a new ester.

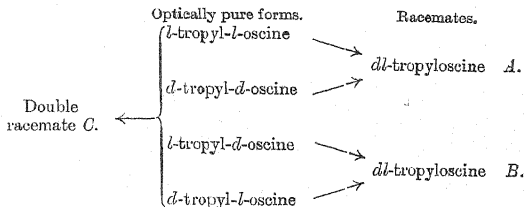
In support of this, some work, which is reserved for future publication, on the re-resolution of racemised *d*-hyoscyne has resulted in the isolation of two esters only, *d*- and *l*-hyoscyne, which is not surprising, as these, being partial racemates, would contain the four expected optically pure forms.

As opposed to the partial racemic ester nature of *d*- and *l*-hyoscines may be cited the rarity of the occurrence of partial racemates in nature, and the novel behaviour of the hyoscines towards *d*-bromocamphorsulphonic acid, which, so far as *d*-hyoscyne is concerned, only resolves *dl* or weakly active hyoscyne as far as the partially racemic ester stage. Although this behaviour is, as far as it has been possible to ascertain, unique, it is only necessary to

recall that in the early days of the application of Pasteur's methods of resolution the formation of partially racemic salts was only rarely observed, whereas at the present time it is recognised as of very frequent occurrence.

At the present stage of the investigation there seem to be only two other possible alternatives, both of which appear rather remote. In the first place, *d*- and *l*-hyoscines may be optically pure forms which, owing to some specific effect of the trotyl group, yield *dl*-osine on hydrolysis, or, secondly, osine may possess a different configuration in the trotyl ester from that in the benzoyl ester and in the free state, whereby the trotyl group is attached to an internally compensated  $\psi$ -osine, which, on hydrolysis, gives rise to a resolvable osine.

*dl*-Hyosine raises a further difficulty, for there are three possible *dl*-hyoscines, as is shown by the following arrangement:



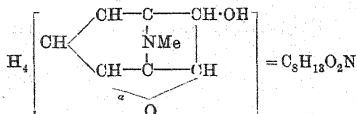
The optically pure forms may be combined in pairs, as indicated, to form two different simple racemates, A and B, or all four forms may be combined to form a double racemate, C. On the acceptance of the partial racemic ester nature of *d*- and *l*-hyoscines, *dl*-hyosine hydrobromide crystallising with three molecules of water, and obtained by crystallising together equal weights of *d*- and *l*-hyosine hydrobromides, constitutes a double racemic salt, the absence of any indication of the presence of another salt and the identical crystalline appearance of *d*- or *l*-hyosine hydrobromide and this salt supporting this view. Moreover, the base crystallising with 2H<sub>2</sub>O is the base contained in this *dl*-salt, as both give the same picrate.

As has already been indicated in the opening paragraph, there is another hydrate of racemic hyosine base, containing 1H<sub>2</sub>O and melting at 56–57°. It was first obtained by Schmidt (*Arch. Pharm.*, 1894, **232**, 409), was re-examined by Luboldt (*ibid.*, 1898, **236**, 11), and more fully investigated by Gadamer (*ibid.*, 382). The last-named investigator showed that the dihydrate can readily

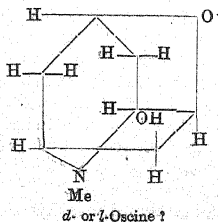
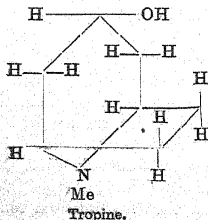
be converted into the monohydrate, but the reverse change was only effected with difficulty. Both hydrates were afterwards described by Hesse (*J. pr. Chem.*, 1901, [ii], **64**, 353), who could not substantiate Gadamer's claims. In reply, Kunz-Krause (*ibid.*, 1901, [ii], **64**, 569) examined Gadamer's three-year-old specimens, and the dihydrate had in every case changed into the base (m. p. 54—55°).

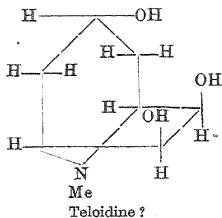
The author has not, so far, been successful in obtaining this monohydrate, so is unable to state with certainty what is the relation between these two racemic hydrates from the point of view of the partial racemic ester nature of *d*- and *l*-hyosine.

The bearing of these results on the structural formula of oscine deserves a passing notice. The most recent and most complete formula is that put forward by Hess (*Ber.*, 1918, **51**, 1007), who ascribes to oscine the structure

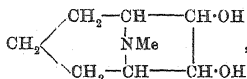


where the linking  $\alpha$  is regarded as being probably attached to one of the carbon atoms of the piperidine nucleus. The experiments on the stability of the active oscines towards racemising agents certainly support this linking. Pyman and Reynolds (T., 1908, **98**, 2077) have pointed out the close relationship which exists between tropine, oscine, and teloidine, all of which contain eight carbon atoms and a hydroxyl group in the molecule. Moreover, their acyl derivatives are found together in *Datura meteloides*. The author is tempted to make the suggestion that, like tropine, the oxygen atom in question in oscine is attached to the  $\gamma$ -position in the piperidine ring. Oscine would therefore be the internal anhydride of a trihydroxytropine, and this trihydroxytropine may be teloidine. The formulæ suggested are:





Teloidine would thus be internally compensated, and in support of this view may be cited the occurrence of meteloidine (tiglyl-teloidine), in nature devoid of optical activity, and the non-resolution of meteloidine by bromocamphorsulphonic acid. Further, Hess (*loc. cit.*) observed that dihydro-oscine, which undoubtedly has the formula



readily produces a silver mirror when treated with ammoniacal silver nitrate solution. The author finds that teloidine and meteloidine, unlike oscine, also readily reproduce this characteristic of dihydro-oscine, the reducing property being probably associated with the adjacent hydroxyl groups, as is found in tartaric acid.

## EXPERIMENTAL.

### *Resolution of Tropic Acid.*

*With Quinine.*—Following the method described by Ladenburg and Hundt (*Ber.*, 1889, **22**, 2591), tropic acid (25 grams) was neutralised to litmus with quinine base (48.8 grams anhydrous) in hot 50 per cent. alcohol. A 49 per cent. yield of a quinine tropate separated. It melted at 176–179°, and had  $[\alpha]_D -126^\circ$  in 95 per cent. alcohol ( $c=1$ ). For further purification it was recrystallised from 95 per cent. alcohol, and, after five crystallisations, 17 grams of quinine *d*-tropate were obtained pure. By working once more through the mother liquors, a further 7.4 grams of pure salt were obtained without difficulty. These two separations combined represent 66 per cent. of the dextro-component.

Quinine *d*-tropate crystallises from 8 parts of boiling alcohol in

groups of radiating needles. In water it is very sparingly soluble. It melts at  $191.5\text{--}192.5^\circ$  ( $195.5\text{--}196.5^\circ$  corr.):

0.1035, dried at  $100^\circ$ , gave 0.2706  $\text{CO}_2$  and 0.0633  $\text{H}_2\text{O}$ .

$\text{C}=71.3$ ;  $\text{H}=6.8$ .

$\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2\cdot\text{C}_9\text{H}_{10}\text{O}_3$  requires  $\text{C}=71.0$ ;  $\text{H}=7.0$  per cent.

The specific rotation was determined in 95 per cent. alcohol.

$c=1.01$ ;  $l=2\text{-dm.}$ ;  $\alpha_D - 2^\circ 18'$ ;  $[\alpha]_D - 113.8^\circ$ .

In absolute alcohol the rotation is smaller.

$c=1.013$ ;  $l=2\text{-dm.}$ ;  $\alpha_D - 2^\circ 6.4'$ ;  $[\alpha]_D - 104.0^\circ$ .

$c=1.002$ ;  $l=2\text{-dm.}$ ;  $\alpha_D - 2^\circ 5.4'$ ;  $[\alpha]_D - 104.3^\circ$ .

As previous observers appeared to have experienced some difficulty in obtaining quinine *l*-tropate in a state of purity, no attempt was made at this stage to isolate this salt. The mother liquors were therefore combined, and the tropic acid containing excess of the *laevo*-component was recovered. Small test samples were converted into the neutral salts with brucine, cinchonine, and quinidine, but although the two former gave crystalline salts, the crystallising power of these was not so pronounced as the salt with quinidine. Accordingly, 3.5 grams of this partly resolved tropic acid were crystallised as quinidine salt, when 4.2 grams of quinidine *l*-tropate were obtained of constant specific rotatory power.

*Resolution with Quinidine and Quinine.*—*dl*-Tropic acid (15 grams) was neutralised with quinidine dissolved in 50 c.c. of 95 per cent. alcohol. On keeping, 22 grams of crystalline material separated. It was obviously a mixture, and had  $[\alpha]_D + 151^\circ$  in 95 per cent. alcohol ( $c=2$ ). After four crystallisations, the specific rotation was constant at  $[\alpha]_D + 145^\circ$ , and the collected quinidine *l*-tropate amounted to 5.5 grams.

*Quinidine l-tropate* crystallises from 95 per cent. alcohol, in which it is soluble in its own weight at  $80^\circ$ , in clusters of well-formed, stout, transparent prisms containing one molecule of water. These exhibit a pronounced heliotrope triboluminescence when powdered in the dark. The air-dried salt when heated in a capillary tube shrinks from about  $110^\circ$ , liquefies between  $118^\circ$  and  $120^\circ$ , and effervesces at  $124^\circ$ . When, however, it is exposed on a watch-glass to a temperature of  $90^\circ$ , it melts completely, and crystallises again on addition of alcohol:

0.2038, air-dried, lost 0.0069 at  $100^\circ$ .  $\text{H}_2\text{O}=3.4$ .

0.1029 " gave 0.2590  $\text{CO}_2$  and 0.0672  $\text{H}_2\text{O}$ .  $\text{C}=68.7$ ;

$\text{H}=7.3$ .

$\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2\cdot\text{C}_9\text{H}_{10}\text{O}_3\cdot\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}=3.5$ ;  $\text{C}=68.5$ ;  $\text{H}=7.1$  per cent.



Its specific rotation was determined in 95 per cent. alcohol, and is dependent on the concentration.

$$c=0.979; l=2\text{-dcm.}; \alpha_D + 2^{\circ}55.2'; [\alpha]_D + 149.1^{\circ}.$$

$$c=1.995; l=2\text{-dcm.}; \alpha_D + 5^{\circ}46.5'; [\alpha]_D + 144.7^{\circ}.$$

The mother liquors were worked up further, and gave an additional 7.2 grams,  $[\alpha]_D + 146^{\circ}$ . This is approximately a 55 per cent. yield of quinidine *l*-tropate. As the liquors now showed no tendency to crystallise at all readily, they were combined, and the tropic acid was recovered by use of ether and hydrochloric acid (10 per cent.). On now crystallising as the quinine salt, after three crystallisations, 14.8 grams of quinine *d*-tropate were obtained pure,  $[\alpha]_D - 114^{\circ}$  ( $c=1$ ), and a further 2.8 grams with  $[\alpha]_D - 115^{\circ}$ . The first mother liquors on concentration deposited quinine *l*-tropate as a homogeneous crop (4.8 grams) of glistening, triangular plates having  $[\alpha]_D - 139^{\circ}$ , and melting at  $184\text{--}185^{\circ}$ . It was recrystallised twice from 95 per cent. alcohol, the specific rotation remaining constant at  $[\alpha]_D - 140.7^{\circ}$  and the melting point at  $185\text{--}186^{\circ}$ , but the form of the crystals changed to needles very similar in appearance to quinine *d*-tropate.

Quinine *l*-tropate melts at  $185\text{--}186^{\circ}$  ( $189\text{--}190^{\circ}$  corr.). It is very much more readily soluble in hot alcohol than is quinine *d*-tropate. The diverse crystalline forms described above do not constitute a case of dimorphism, but merely represent extreme crystalline forms. By suitably modifying the conditions of crystallisation, a series of intermediate forms may be obtained consisting of more or less elongated trapezoidal plates. Unlike quinine *d*-tropate, this salt exhibits a very faint triboluminescence, the intensity of which is not visibly affected by the form of the crystals:

0.1083, dried at  $100^{\circ}$ , gave 0.2817  $\text{CO}_2$  and 0.0668  $\text{H}_2\text{O}$ .

$\text{C}=71.0$ ;  $\text{H}=6.9$ .

$\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2\text{C}_6\text{H}_{10}\text{O}_3$  requires  $\text{C}=71.0$ ;  $\text{H}=7.0$  per cent.

The tropic acid contained in the residual liquors was reconverted into the quinidine salt, when 4.3 grams of quinidine *l*-tropate were obtained, having  $[\alpha]_D + 145^{\circ}$ . The residual solution was not further examined.

By the use of the two bases quinidine and quinine, there were thus isolated in an approximate state of purity 88 per cent. of quinine and quinidine *l*-tropates and 80 per cent. of quinine *d*-tropate. The proportion of tropic acid resolved is 84 per cent.

Quinidine *d*-tropate was not isolated, but, on keeping in the ice-chest, a small crop of white, woolly needles separated from the

mother liquors (together with quinidine *l*-tropate), which was probably this salt in an impure condition.

#### *d*-Tropic Acid.

Pure quinine *d*-tropate (16 grams) was acidified with 50 c.c. of 5 per cent. hydrochloric acid and completely extracted with purified ether. The crude acid so obtained (5.1 grams) melted at 127—128°, and had  $[\alpha]_D + 77.2^\circ$  in water ( $c=1$ ). On recrystallisation from water, the melting point rose to 128—129°, and the rotation to  $[\alpha]_D + 79^\circ$ . After two more crystallisations, the melting point remained unchanged, but the rotation rose to  $[\alpha]_D + 81.6^\circ$ . The yield was 3.1 grams.

*d*-Tropic acid crystallises from water in delicate, lustrous scales, which become transformed on keeping in contact with the solution into elongated prisms of hexagonal cross-section. Both forms melt at 128—129° (129—130° corr.) and are anhydrous:

0.2014 was equivalent to 11.9 c.c. *N*/10-baryta.

M.W.=169.  $C_9H_{10}O_3$  requires M.W.=166.

The specific rotation was determined in alcohol and in water.

In water:

$$c=1.027; l=2\text{-dcm.}; \alpha_D + 1^\circ 40' 6''; [\alpha]_D + 81.6^\circ.$$

In absolute alcohol:

$$c=0.997; l=2\text{-dcm.}; \alpha_D + 1^\circ 24' 2''; [\alpha]_D + 70.3^\circ.$$

$$c=2.472; l=2\text{-dcm.}; \alpha_D + 3^\circ 33' 1''; [\alpha]_D + 71.8^\circ.$$

The specific rotation of the ion was determined by dissolving 0.200 gram of *d*-tropic acid and 0.0638 gram of anhydrous sodium carbonate in water and making up to 20 c.c. The dissolved carbon dioxide was not removed:

$$l=2\text{-dcm.}; \alpha + 1^\circ 22' 9''; [\alpha]_D \text{ for ion} + 69.4^\circ; [M]_D \text{ for ion} + 114.7^\circ.$$

Gadamer (*Arch. Pharm.*, 1901, **239**, 294) has previously noted a fall of rotation of *l*-tropic acid on converting into a salt, but has not followed it quantitatively.

#### *l*-Tropic Acid.

*From Quinidine l*-Tropate.—Four grams of pure quinidine *l*-tropate, on treatment with hydrochloric acid (10 per cent.) and extraction with ether, gave 1.35 grams of *l*-tropic acid, which, after three crystallisations from water, gave 0.5 gram melting at 128—129° (129—130° corr.). The specific rotatory power was determined in water, and was slightly less than that of the purest *d*-tropic acid:

$$c=0.995; l=2\text{-dcm.}; \alpha_D - 1^\circ 37'; [\alpha]_D - 81.2^\circ.$$

*From Quinine l-Tropate.*—5.8 Grams of this salt gave 2.0 grams of *l*-tropic acid, which was recrystallised four times from water, giving 1.35 grams melting at 128—129°, and with a specific rotation  $-81.2^\circ$ :

$$c=1.002; l=2\text{-dm.}; \alpha_D -1^\circ 37.6'; [\alpha]_D -81.2^\circ.$$

*l*-Tropic acid prepared in this way had the same general properties as the dextro-acid. It is very sparingly soluble in cold benzene, but freely so in cold methyl ethyl ketone or ethyl acetate. From the latter solvent, it crystallises exceedingly well in clear tablets:

0.1775 was equivalent to 11.72 c.c. *N*/10-baryta.

M.W.=168.  $C_9H_{10}O_3$  requires "M.W.=166.

### *The Resolution of Oscine.*

*Partial Racemate with d- $\alpha$ -Bromo- $\pi$ -camphorsulphonic Acid.*—Two and a-half grams of oscine were converted into this salt, which was very conveniently recrystallised from absolute alcohol. The first crop of crystals weighed 4.9 grams, melted at 232°, and gave  $[\alpha]_D +58.8^\circ$  in water ( $c=2$ ). It was recrystallised twice more from absolute alcohol, yielding, finally, 3.6 grams melting at 232—233°. The specific rotation determined in water was practically unchanged:

$$c=2.001; l=2\text{-dm.}; \alpha_D +2^\circ 32.4'; [\alpha]_D +59.3^\circ; [M]_D +276.7^\circ.$$

The value for the molecular rotation  $276.7^\circ$  is in good agreement with the molecular ionic value 278.7 for bromocamphorsulphonic acid (Pope and Read, T., 1910, 97; 2200).

*dl-Oscine d- $\alpha$ -bromo- $\pi$ -camphorsulphonate* crystallises exceedingly well from absolute alcohol in clear, diamond-shaped plates. Ten parts by volume of boiling absolute alcohol are required to dissolve one part by weight of the salt. It melts at 232—233° (237—238° corr.):

0.0995, dried at 100°, gave 0.1703  $CO_2$  and 0.0526  $H_2O$ .

C=46.69; H=5.91.

$C_8H_{13}O_2N, C_{10}H_{15}O_4BrS$  requires C=46.34; H=6.05 per cent.

*Behaviour with d- $\alpha$ -Bromo- $\beta$ -camphorsulphonic Acid.*—Six and a-half grams of oscine were combined with an equivalent of *d- $\alpha$ -bromo- $\beta$ -camphorsulphonic acid*. The salt could not be obtained crystalline either from water or from a mixture of ethyl acetate and absolute alcohol. A very concentrated solution of the salt in absolute alcohol, however, crystallised as a cake of needles on keeping for a prolonged time in the ice-chest. It was too readily soluble for systematic fractionation from absolute alcohol, and the addition of dry ethyl acetate unexpectedly prevented crystallisa-

tion. The first crop of crystals from absolute alcohol was collected, and weighed 8.7 grams. It melted at 150—155°, and its specific rotation was determined in water:

$$c=2.00; l=2\text{-dcm.}; \alpha_D + 2^\circ 27.4'; [\alpha]_D + 61.4^\circ; [M]_D + 286.3^\circ.$$

This product was recrystallised from absolute alcohol, but in the meantime tartaric acid had effected the resolution of oscine quite simply, so the investigation of the above salt was discontinued.

*With Camphor- $\beta$ -sulphonic Acid.*—Attempts to crystallise this salt were ineffective.

*Resolution by d-Tartaric Acid.*—*dl*-Oscine (13.9 grams) was converted into its *d*-hydrogen tartrate by addition of 13.5 grams of *d*-tartaric acid in aqueous solution. The solution was concentrated to a low bulk, and gave 13.8 grams of a salt crystallising in hexagonal plates and with a specific rotation  $[\alpha]_D + 3.5^\circ$  in water. After one more crystallisation, it gave 10.2 grams and had  $[\alpha]_D + 1.1^\circ$ . This value was not appreciably altered by subsequent repeated crystallisation, and represents the optical constant of the salt *l*-oscine *d*-hydrogen tartrate.

*l*-Oscine *d*-hydrogen tartrate crystallises with one molecule of water of crystallisation in large and clear octahedra. Very often these have a flattened appearance, and, more rarely, one-half the faces may be almost entirely suppressed, with the formation of tetrahedra. Unbroken crystals melt at 134° with effervescence, but when powdered partly melt at about 130° and gradually liquefy up to 160°. The anhydrous material melts at 173—174° (176.5—177.5° corr.). It is readily soluble in cold water, but the crystals can be washed with 50 per cent. alcohol with little loss. From dilute alcoholic solutions, this salt tends to separate as an oil:

0.3126, dried at 105°, lost 0.0181.  $\text{H}_2\text{O}=5.8$ .

$\text{C}_8\text{H}_{13}\text{O}_2\text{N}, \text{C}_4\text{H}_6\text{O}_6, \text{H}_2\text{O}$  requires  $\text{H}_2\text{O}=5.6$  per cent.

0.1159, dried at 100°, gave 0.1996  $\text{CO}_2$  and 0.0690  $\text{H}_2\text{O}$ .

$\text{C}=47.0; \text{H}=6.7$ .

$\text{C}_8\text{H}_{13}\text{O}_2\text{N}, \text{C}_4\text{H}_6\text{O}_6$  requires  $\text{C}=47.2 \text{ H}=6.3$  per cent.

The specific rotation was determined in water:

$$c=2.007; l=2\text{-dcm.}; \alpha_D + 2.56'; [\alpha]_D + 1.06^\circ.$$

The average value, for nine different samples of the pure salt, of  $[\alpha]_D$  was  $+1.29^\circ$ , the extremes being  $+0.93^\circ$  and  $+1.56^\circ$ . Taking this average value for  $[\alpha]_D$ , the molecular rotation  $[M]_D$  is calculated as  $+4.18^\circ$ , and employing Landolt's value (*Ber.*, 1873, 6, 1075) for the molecular rotation of ammonium hydrogen tartrate,

+42.84°, the value for the *l*-oscinium ion is  $[M]_D - 38.66^\circ$ , whence  $[\alpha]_D - 24.7^\circ$ .

On continuing the fractionation of the mother liquors, 71 per cent. of the *l*-oscine *d*-hydrogen tartrate present was isolated in a state of purity. The separation was materially accelerated by inoculation of the less mobile solutions, followed by addition of alcohol in insufficient amount to precipitate an oil. The residual solutions, now relatively rich in *d*-oscine *d*-hydrogen tartrate, were concentrated to a syrup, and, on allowing to remain in a desiccator exposed to a dehydrating agent, crystallised as a striated mass of crystals. These were collected, freed from the adhering syrupy mother liquor, first by suction and then by very limited use of 50 per cent. alcohol as a washing agent. The salt was a monohydrate, and gave  $[\alpha]_D + 23.7^\circ$ . It was recrystallised from water, and separated under similar conditions as a felted mass of needles. These now gave  $[\alpha]_D + 27.3^\circ$  (anhydrous).

*d*-Oscine *d*-hydrogen tartrate monohydrate melts from 55° to 65°, forming a meniscus at the latter temperature. It readily effloresces when exposed to the atmosphere, and when dehydrated in a vacuum over sulphuric acid loses its water of crystallisation. The anhydrous material still melts at 55—65°. This is probably the melting point of an amorphous form, as, on keeping, it acquires the melting point of the crystalline anhydrous salt, namely, 163—165° (see below).

Three different samples of the salt were analysed for their water content. The first, representing a freshly collected salt, gave the following result:

0.4502, dried over  $H_2SO_4$ , lost 0.0320.  $H_2O = 7.1$ ;

and a salt which showed some signs of efflorescence gave the following:

0.2023 lost 0.0091.  $H_2O = 4.5$ .

$C_8H_{13}O_2N, C_4H_6O_6, H_2O$  requires  $H_2O = 5.6$  per cent.

On keeping for some time, this salt had completely effloresced: 0.1180, dried at 100°, lost nil.

0.1180, dried at 100°, gave 0.2055  $CO_2$  and 0.0649  $H_2O$ .  
C = 47.5; H = 6.15.

$C_8H_{13}O_2N, C_4H_6O_6$  requires C = 47.2; H = 6.3 per cent.

The specific rotation of the dehydrated salt was determined in water:

$c = 0.949$ ;  $l = 2$ -dm.;  $\alpha_D + 31.1'$ ;  $[\alpha]_D + 27.3^\circ$ .

When the hydrated salt is washed with absolute alcohol, it is transformed into a white, crystalline powder, which is the

anhydrous salt and the stable form at the ordinary temperature. When crystallised from water, the anhydrous salt separates from a syrupy solution very slowly in large, hexagonal-shaped tablets, which, unlike the hydrated salt, can be washed freely with 50 per cent. alcohol. If a syrupy solution is inoculated with a trace of both forms, hydrated and anhydrous, the hydrated form crystallises first, filling the liquid space, and, on keeping, disappears entirely, being replaced by the stable, anhydrous form. For the isolation of pure *d*-oscine *d*-hydrogen tartrate, the latter form is the more convenient. The process is, however, very slow, owing to the solubility of *d*-oscine *d*-hydrogen tartrate and the slow velocity of crystallisation from viscous solutions.

*d*-Oscine *d*-hydrogen tartrate melts at 167—168° (170—171° corr.).

The specific rotation was determined in water and for a salt which had been crystallised to constant rotation:

$$c = 1.016; l = 2\text{-dm.}; \alpha + 34'; [\alpha]_D + 27.87^\circ; [M]_D + 85.17^\circ.$$

This gives a value +42.3° for the molecular rotation of the *d*-oscinium ion and  $[\alpha] + 27.10^\circ$ . This is somewhat greater numerically than the value  $[\alpha]_D - 24.7$  obtained by a similar calculation for the *l*-oscinium ion. As this is beyond the limits of experimental error, it is probably another example of the phenomenon first drawn attention to by Pope and Read (T., 1912, 101, 760), who show conclusively that the molecular rotatory power in aqueous solution of certain salts of the type *l*-base *d*-acid is in agreement with the value calculated from the separate ions, but that the combination *d*-base *d*-acid gives an abnormal value.

*l*-Oscine Picrate.—Six grams of pure *l*-oscine *d*-hydrogen tartrate were added to a boiling saturated solution of 4.25 grams of picric acid in 80 c.c. of water. As the solution cooled, the major portion of the salt crystallised in long needles, but when only luke-warm a denser form appeared in the shape of small, modified rhombs. The yield was 6.35 grams and the melting point 237° (decomp.). The combined product was recrystallised from 35 c.c. of hot water, and, on removing the source of heat, separated at once in long, glistening needles. These were collected while the solution was still warm, the filtrate continuing to deposit solely needles for some time, and then rhombs. The filtrate was heated to dissolve all the crystals, and when cold only deposited the rhomb-like form of crystal, which closely resembles *dl*-oscine picrate. The yield of needles was 4.95 grams, melting at 237—238° (decomp.) (242.5—243.5° corr.), whilst the rhombs amounted to 0.95 gram, and also melted at 237—238° (decomp.). Both forms are

anhydrous, and either form when mixed with *dl*-oscine picrate, which itself also melts at 237—238°, shows no depression of the melting point. At the ordinary temperature, the needle form of picrate is certainly the unstable one, as is readily shown by adding a drop of saturated picric acid solution to a few small crystals of *l*-oscine *d*-hydrogen tartrate and rubbing with a glass rod. The crystals dissolve instantly, and a homogeneous crop of needles first makes its appearance, followed quickly by minute rhombs, and in a short time the needles will have entirely disappeared, their disintegration and solution being readily followed with the aid of a microscope. This behaviour is useful as a test as to whether one is dealing with active or *dl*-oscine salts, since *dl*-oscine picrate has always been observed to separate in small, flattened rhombs.

*l*-Oscine Hydrochloride.—Four grams of *l*-oscine picrate (needle form) were decomposed by shaking with three molecular proportions of 5 per cent. hydrochloric acid, and the picric acid was removed by ether. The solution of the *l*-oscine hydrochloride was completely dehydrated by repeated evaporation to dryness with absolute alcohol, leaving, finally, a white, crystalline powder, which was dissolved in 10 c.c. of boiling absolute alcohol. On keeping, *l*-oscine hydrochloride separated in aggregates of small prisms in the form of warts; a few isolated prisms were also present. The product was collected, and amounted to 1.4 grams. It melted and decomposed at 273—274° (281—282° corr.). A mixture with *dl*-oscine hydrochloride (m. p. 273—274°) also melted at the same temperature. Unlike *dl*-oscine hydrochloride, the *laevo*-salt is very highly deliquescent. A direct comparison of the two was made by exposing a few crystals of each on watch-glasses to the atmosphere. In a few minutes, the *laevo*-salt had completely liquefied, whilst the *dl*-salt was apparently unaffected. On keeping for an hour, however, the latter showed signs of deliquescence, and the deliquesced salt recrystallised in well-formed tablets melting partly at about 100°, and probably representing the monohydrated *dl*-oscine hydrochloride described by Luboldt (*Arch. Pharm.*, 1898, 236, 18).

The specific rotation of *l*-oscine hydrochloride was determined in water, employing a salt which had been dried at 100°:

$c = 0.997$ ;  $l = 2\text{-dm.}$ ;  $\alpha = -23.6'$ ;  $[\alpha]_D = -19.71^\circ$ ;  $[M]_D = -37.76^\circ$ ; whence  $[\alpha]_D$  for the *l*-oscinium ion is  $-24.2^\circ$ , whereas the value calculated from the molecular rotation of *l*-oscine *d*-hydrogen tartrate was  $-24.7^\circ$ .

*l*-Oscine Hydrochloride from *l*-Oscine Picrate (Rhombs).—As has been indicated above, *dl*-oscine picrate and *l*-oscine picrate melt at the same temperature, and the stable modification of

*l*-oscine picrate crystallises very similarly to *dl*-oscine picrate. It was therefore necessary to prove that this stable form of *l*-oscine picrate did actually contain the active base. Accordingly, 0.5 gram of *l*-oscine picrate (rhombs) was converted as quantitatively as possible by means of ether and three molecular proportions of *N*/10-hydrochloric acid into *l*-oscine hydrochloride. The solution was concentrated somewhat and made up to 20 c.c. In a 2-dcm. tube the observed rotation was  $\alpha_D - 25.3'$ , from which it is calculated that the *l*-oscinium ion has  $[\alpha]_D - 21^\circ$ , a value in good agreement with that observed directly for *l*-oscinium hydrochloride. The solution was then dried, and the hydrochloride recrystallised from alcohol. It gave 0.11 gram of highly deliquescent *l*-oscine hydrochloride melting at  $271-272^\circ$ , and when tested with saturated picric acid solution gave the unstable needle form of *l*-oscine picrate, changing into rhombs.

*l*-Oscine Base.—To avoid the action of alkalis, which it was thought might cause partial racemisation, *l*-oscine base was prepared as follows. *l*-Oscine picrate (4.75 grams) was treated with three equivalents of dilute sulphuric acid solution, and the picric acid removed by purified ether. After treating with charcoal to remove the last traces of picric acid, the solution was concentrated under diminished pressure to about 20 c.c., and excess of pure barium carbonate added. On allowing to remain overnight, the solution was free from sulphation, and only contained *l*-oscine partly present as carbonate. The major portion of the *l*-oscine was readily removed by extraction with freshly purified chloroform, the remainder being retained by the dissolved carbon dioxide. When the latter solution was evaporated to dryness in a vacuum over sulphuric acid and redissolved in a little water, the rest of the oscine was readily extracted by chloroform. In this way, the *l*-oscine was recovered quantitatively as base. The first chloroform extract on complete removal of the solvent crystallised at once. The product was white and amounted to 1.45 grams. It had a specific rotatory power of  $[\alpha]_D - 52.8^\circ$  in water. It melted at  $109-110^\circ$ , the same as *dl*-oscine, whilst a mixture of the two showed no depression of the melting point. When recrystallised from light petroleum, it separated in long needles. The melting point was unchanged at  $109.5-110.5^\circ$  (corr.).

The specific rotatory power was determined in water:

$$c = 1.010; l = 2\text{-dcm.}; \alpha = -1^\circ 3.6'; [\alpha]_D - 52.4^\circ.$$

With Mayer's reagent (potassium mercuric iodide), *l*-oscine base gives no precipitate, but in the form of a salt it gives a crystal-



line precipitate. The presence of a slight excess of acid prevents the separation of crystals. *dl*-Oscine behaves similarly.

*Action of Acids and Alkalis on l-Oscine.*—A solution of 0.2 gram of *l*-oscine in water having an observed rotation of  $\alpha_D -1^\circ 1.7'$  in a 2-dcm. tube was treated with one drop (0.04 c.c.) of 50 per cent. potassium hydroxide solution. After nineteen hours, the observed rotation was unchanged,  $\alpha_D -1^\circ 1.5'$ .

The same solution was heated on the boiling-water bath for an hour. At the end of this period, the rotation was still  $-1^\circ 1.7'$ . Five c.c. of 50 per cent. potassium hydroxide were now added, and the solution was boiled for an hour. Making a correction for the change in volume, the observed rotation was unchanged,  $\alpha_D -1^\circ 1.2'$ . This means that 0.2 gram of *l*-oscine was not racemised by boiling for an hour with excess of 10 per cent. potassium hydroxide solution.

There was, however, partial racemisation when 0.2 gram of *l*-oscine was heated with 15 c.c. of saturated baryta solution for four hours at  $150^\circ$ , the value of  $[\alpha]_D$  having fallen to about one-half its original value.

The action of boiling 10 per cent. hydrobromic acid also failed to racemise *l*-oscine, for 1 gram of *l*-oscine *d*-hydrogen tartrate in 30 c.c. of 10 per cent. hydrobromic acid had an observed rotation,  $\alpha_D -21.1'$ , in a 2-dcm. tube, and after three hours' boiling the rotation was practically unaltered,  $\alpha_D -22.6'$ .

*d-Oscine Base.*—One gram of pure *d*-oscine *d*-hydrogen tartrate was dissolved in 10 c.c. of 5 per cent. sodium hydroxide solution, and the base extracted with purified chloroform. The combined extracts were clarified by shaking with anhydrous potassium carbonate, filtered, and the solvent removed by distillation. The residual base crystallised instantaneously throughout on touching one spot with a glass rod. A similar very high velocity of crystallisation had previously been noticed with the chloroform-free *laevo*-oscine base. It was crystallised from light petroleum, and separated in long, radiating needles, often forming fasciated growths. It melted at  $109$ – $110^\circ$  ( $109.5$ – $110.5^\circ$  corr.), and a mixture with pure *dl*-oscine also at the same temperature.

Its specific rotation was determined in water:

$$c=1.029; l=2\text{-dcm.}; \alpha_D +1^\circ 7.6'; [\alpha]_D +54.8^\circ.$$

*d-Oscine Picrate.*—The solution of the base which had been used for determining the rotatory power was treated with an equivalent of picric acid (0.3 gram) and rapidly concentrated to about 10 c.c. On allowing to cool, long, radiating, glistening needles of *d*-oscine

picrate (0.3 gram) separated. These melted at  $237\text{--}238^{\circ}$  ( $242.5\text{--}243.5^{\circ}$  corr.). The mother liquors were concentrated, and, when quite cold, the stable dimorph separated in small, flattened rhombs exactly as observed in the case of *l*-oscine picrate. This form also melted at  $237\text{--}238^{\circ}$ . A mixture with *d*-oscine picrate, obtained by acid hydrolysis of benzoyl-*d*-oscine, also melted at the same temperature.

*d*-Oscine Hydrochloride.—To complete the analogy with the *l*-acvo-series, this salt was prepared and its specific rotation determined. For this purpose, 0.2078 gram of *l*-oscine base was neutralised with the calculated quantity, 13.4 c.c., of *N*/10-hydrochloric acid, and the volume made up to 20 c.c. In a 2-dcm. tube was found  $\alpha_D$   $30.1'$ , whence  $[\alpha]_D$  for the *d*-oscinium ion is  $+24.0^{\circ}$ , a value in agreement with  $[\alpha]_D - 24.2^{\circ}$  observed for the *l*-oscinium ion.

The solution just employed was evaporated to dryness and the residue crystallised from absolute alcohol, when *d*-oscine hydrochloride separated in warts with a few isolated prisms. The melting point was  $273\text{--}274^{\circ}$ , and the salt was very deliquescent.

#### *Resolution of Benzoyloscine.*

This was effected substantially as described by Tutin (T., 1910, 97, 1793).

Five grams of *dl*-oscine hydrobromide were converted into the base, which was heated to  $160^{\circ}$  with 10 c.c. of benzoyl chloride, when a brisk reaction ensued with simultaneous crystallisation of the benzoyloscine hydrochloride. The solid was collected, washed with ether, and dried at  $100^{\circ}$ . The crude product melted at  $240^{\circ}$  and amounted to 5.45 grams, that is, an 83 per cent. yield. It was dissolved in water, and the solution, after decolorisation with a little charcoal, was rendered alkaline with sodium hydrogen carbonate, and completely extracted with chloroform. The benzoyloscine left on removing the chloroform was neutralised to litmus with *d*- $\alpha$ -bromo- $\pi$ -camphorsulphonic acid, and the salt fractionated from absolute alcohol. The *d*-benzoyloscine bromo-camphorsulphonate was obtained pure after three crystallisations, and melted at  $247\text{--}248^{\circ}$  (Tutin gives  $246\text{--}246.5^{\circ}$ ). The specific rotation was determined in water:

$c = 1.998$ ;  $l = 2\text{-dcm.}$ ;  $\alpha_D + 2^{\circ}11.3'$ ;  $[\alpha]_D + 54.74^{\circ}$ ;  $[M]_D + 312.3^{\circ}$ .

The calculated value of the molecular rotatory power of the *d*-benzoyloscinium ion is therefore  $312.3 - 278.7 = 33.6^{\circ}$ , whence  $[\alpha]_D$  for the *d*-benzoyloscinium ion is  $+12.9^{\circ}$ .

*Benzoyl-d-oscine Hydrochloride.*

Pure benzoyl-*d*-oscine bromocamphorsulphonate (2.8 grams) was triturated with 30 c.c. of water and three molecular proportions of sodium hydrogen carbonate. Benzoyl-*d*-oscine base appeared to separate in needles, which were immediately dissolved by chloroform. The free base, on removal of the solvent, was exactly neutralised with *N*/10-hydrochloric acid, and, after filtering from a little greasy matter, was concentrated rapidly under diminished pressure to a very small volume. On keeping for a short time, the whole of the liquid became filled with perfectly formed rectangular leaflets, which in a few hours were completely transformed into fine needles. These were collected and washed with absolute alcohol. They amounted to 1.1 grams, and melted and decomposed at 280° (287° corr.) (Tutin gives 283—284°). The product was anhydrous. Its specific rotation was determined in dilute aqueous solution:

$c = 2.005$ ;  $l = 2$ -dcm.;  $\alpha_D + 28.35'$ ;  $[\alpha]_D + 11.79^\circ$ ;  $[M]_D + 34.83^\circ$ .

From this is calculated  $[\alpha]_D + 13.4^\circ$  for the benzoyl-*d*-oscinium ion, a value which compares favourably with the value  $+12.9^\circ$  calculated above from the bromocamphorsulphonate. This value is somewhat higher than Tutin's value,  $[\alpha]_D + 10.0^\circ$ , which is obtained by calculation from the value  $[M]_D + 297.0^\circ$  for benzoyl-*d*-oscine bromocamphorsulphonate.

*Hydrolysis of Benzoyl-d-oscine.*

*With Hydrochloric Acid.*—The solution just employed (20 c.c.), containing 0.4001 gram of benzoyl-*d*-oscine hydrochloride, was treated with 9.7 c.c. of 31 per cent. hydrochloric acid, thus bringing the volume approximately to 30 c.c. and the strength of the acid to 10 per cent. The rotation was observed, and the solution was then boiled gently to hydrolyse the benzoyl-*d*-oscine, the rotation being observed at intervals, just as is described under the hydrolysis of *L*-hyosine (p. 507).

Initial reading,  $+20'$ ;  $l = 2$ -dcm.

After 1 hour's boiling,  $+20.5'$ .

After 3 hours' boiling,  $+22.0'$ .

Hydrolysis was now complete, as there was a copious separation of benzoic acid, and the solution gave no turbidity with Mayer's reagent. The observed rotation is therefore due to the *d*-oscinium ion, and the final value,  $+22'$ , corresponds with a specific rotation of the *d*-oscinium ion of  $+26^\circ$ , which is of the same order as that

obtained by calculation from the rotation of *d*-oscine *d*-hydrogen tartrate, namely,  $[\alpha]_D$  27.1°, and that directly observed,  $[\alpha]_D$  24.0°, for *d*-oscinium hydrochloride prepared from the tartrate.

The free benzoic acid was removed by extraction with purified ether, and the aqueous liquor concentrated to a syrup under diminished pressure on the water-bath. On dehydration of the syrup by evaporation with absolute alcohol, the residue crystallised. It was dissolved in a little hot absolute alcohol, and, on keeping, 0.07 gram of crystals resembling ammonium chloride were collected. They melted and decomposed in the neighbourhood of 243° (pure *d*-oscine hydrochloride melts at 273°), and were highly deliquescent.

Twenty milligrams of this salt, when treated with an equal weight of picric acid in hot aqueous solution, gave a picrate crystallising in long, fine needles, and later a few rhombs separated, a behaviour which is exactly reproduced by the addition of picric acid solution to the pure *d*- or *l*-oscine *d*-hydrogen tartrates (p. 495). This picrate, when collected and dried, melted and decomposed at 237—238°. A mixture with *d*-oscine picrate melted in the same bath at 237—238°. The alcoholic mother liquors of the above 0.07 gram of *d*-oscine hydrochloride were combined with picric acid (both in aqueous solution). The addition of the picric acid first precipitated amorphous matter, which was separated, and later a well-crystallised picrate. This salt crystallised in small rhombs, melted and decomposed at 235°, and was in all probability the stable form of *d*-oscine picrate.

*With Alkali.*—Pure benzoyl-*d*-oscine hydrochloride (0.4009 gram) was dissolved in water, and 5 c.c. of 10 per cent. sodium hydroxide were added. The oily base, which separated rapidly, disappeared on boiling. After an hour, the solution was cooled and neutralised to Congo paper with hydrochloric acid. The precipitated benzoic acid was completely removed by ether extraction, and the extracted aqueous liquor was also free from non-hydrolysed benzoyloscine, as was indicated by the absence of a turbidity on treatment with Mayer's reagent in acid solution. In neutral or very faintly acid solution it gave the well-crystallised precipitate observed with oscine salts. The solution was rapidly concentrated and made up to 20 c.c. In a 2-dcm. tube it gave  $\alpha_D + 32.8'$ , whence the *d*-oscinium ion has  $[\alpha]_D + 25.8^\circ$ , a value in good agreement with that observed by acid hydrolysis,  $[\alpha]_D + 26.0^\circ$ , and that observed for pure *d*-oscine hydrochloride,  $[\alpha]_D + 24.0^\circ$ .

*d-Hyoscine.*

The starting material for the isolation of *d*-hyoscine consisted of 75 grams of well-crystallised hydrobromides obtained as a by-product in the manufacture of *l*-hyoscine. It was slightly levorotatory, having  $[\alpha]_D -4.1^\circ$  ( $c=2.3$ , anhydrous), and contained 9 per cent. of water of crystallisation, which was lost over sulphuric acid. It was regenerated to base, using sodium hydrogen carbonate and chloroform for the purpose, the weight of base being about 55 grams. This was converted into its salt with *d*- $\alpha$ -bromo- $\pi$ -camphorsulphonic acid, and crystallised from a mixture of dry ethyl acetate and absolute alcohol. In a few days there was a copious, crystalline separation, which was collected, and amounted to 38.5 grams. It was deliquescent and had  $[\alpha]_D +46.4^\circ$  ( $c=2$ ), and on two more crystallisations gave 8.8 grams of pure meteloidine bromocamphorsulphonate.

*Meteloidine d- $\alpha$ -bromo- $\pi$ -camphorsulphonate* crystallises exceedingly well from absolute alcohol, in which it is soluble to the extent of about 1 part in 10 (boiling), or from a mixture with dry ethyl acetate in clusters of prisms. It also crystallises well from water. It melts at  $224-227^\circ$  ( $228.5-231.5^\circ$  corr.), and is anhydrous:

0.1410 gave 0.2547  $\text{CO}_2$  and 0.0808  $\text{H}_2\text{O}$ .  $\text{C}=49.3$ ;  $\text{H}=6.4$ .

$\text{C}_{13}\text{H}_{21}\text{O}_4\text{N}$ ,  $\text{C}_{10}\text{H}_{15}\text{O}_4\text{BrS}$  requires  $\text{C}=48.75$ ;  $\text{H}=6.4$  per cent.

Its specific rotatory power was determined in water:

$c=2.039$ ;  $l=2\text{-dm.}$ ;  $\alpha_D +1^\circ 56'$ ;  $[\alpha]_D +47.42^\circ$ ;  $[\text{M}]_D +268.7^\circ$ .

This value for the molecular rotation is somewhat smaller than that given by Pope and Read for the bromocamphorsulphonic acid ion (T., 1910, 97, 2200). That the meteloidine was inactive was confirmed in two ways:

(1) A small quantity of the above salt was converted into base, avoiding conditions which might favour racemisation by using sodium hydrogen carbonate and chloroform. The base crystallised readily, and was identical in appearance and other properties with a sample of meteloidine kindly supplied by Dr. Pyman, and which was known to be inactive (Pyman and Reynolds, T., 1908, 93, 2077).

(2) One-half a gram of *i*-meteloidine base was converted into its bromocamphorsulphonate, and the solution evaporated to dryness with absolute alcohol. The crystalline residue was triturated with a little dry ethyl acetate, in which the crystals are practically insoluble, and collected. The rotation of this salt, representing

practically the whole of the meteloidine, was found to be the same as the previously described salt:

$c=1.969$ ;  $l=2\text{-dcm.}$ ;  $\alpha+1^{\circ}51'$ ;  $[\alpha]_D+47.0^{\circ}$ ;  $[M]_D+266.3^{\circ}$ .

It melted at  $224\text{--}225^{\circ}$ , and a mixture of the two salts showed no depression of the melting point.

*Isolation of d-Hyoscine Bromocamphorsulphonate.*—On continuing the fractionation, the original mother liquors gave a second crop of crystals, 24.5 grams,  $[\alpha]_D+44.5^{\circ}$ , which, after ten recrystallisations, gave 11.6 grams of pure *d*-hyoscine bromocamphorsulphonate melting at  $159\text{--}160^{\circ}$  and having  $[\alpha]_D+60.1^{\circ}$ . This was twice more recrystallised, and gave 8.3 grams with  $[\alpha]_D+60.3^{\circ}$ .

*d-Hyoscine d- $\alpha$ -bromo- $\pi$ -camphorsulphonate* crystallises from a mixture of absolute alcohol and excess of dry ethyl acetate in clusters of glistening, acicular needles. After being dried at  $110^{\circ}$  it melts at  $158\text{--}160^{\circ}$  ( $161.5\text{--}163.5^{\circ}$  corr.). Its specific rotation was determined in water at  $16^{\circ}$ .

$c=2.005$ ;  $l=2\text{-dcm.}$ ;  $\alpha+2^{\circ}25'$ ;  $[\alpha]_D+60.3^{\circ}$ ;  $[M]_D+370.5^{\circ}$ .

From this it is calculated that the molecular rotatory power of the *d*-hyoscinium ion is  $91.8^{\circ}$  and the specific rotatory power  $[\alpha]_D$  is  $+30.2^{\circ}$  (see *d*-hyoscine hydrobromide). The salt is not deliquescent:

0.2730 lost 0.0022 at  $100^{\circ}$ . Loss = 0.8.

0.1238, dried at  $100^{\circ}$ , gave 0.2394  $\text{CO}_2$  and 0.0675  $\text{H}_2\text{O}$ .

$\text{C}=52.8$ ;  $\text{H}=6.1$ .

$\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}, \text{C}_{10}\text{H}_{15}\text{O}_4\text{BrS}$  requires  $\text{C}=52.7$ ;  $\text{H}=5.9$  per cent.

The fractionation of the various liquors was continued, when further small quantities, 4.5 grams in all, of meteloidine bromocamphorsulphonate, and an additional 12.5 grams of pure *d*-hyoscine bromocamphorsulphonate,  $[\alpha]_D+60.5^{\circ}$ , were obtained. The original mother liquors now gave 10 grams of a deliquescent salt,  $[\alpha]_D+30.8^{\circ}$ , and 2.7 grams,  $[\alpha]_D+27.3^{\circ}$ , both of which had the properties of a slightly impure *l*-hyoscine bromocamphorsulphonate, which requires a calculated value of  $[\alpha]_D+29^{\circ}$ . On recrystallisation, these gave salts of higher specific rotation. It was not found possible to isolate pure *l*-hyoscine bromocamphorsulphonate from the mother liquors.

*d-Hyoscine Hydrobromide.*—Six grams of pure *d*-hyoscine bromocamphorsulphonate were converted into base, using chloroform and sodium hydrogen carbonate for the regeneration. The base was neutralised with hydrobromic acid and the solution concentrated under diminished pressure. *d*-Hyoscine hydrobromide separated on keeping in large tablets ( $2 \times 1\text{ cm.}$ ).

*d-Hyoscyne hydrobromide* crystallises exceedingly well from water in rectangular-shaped tablets with bevelled edges. It crystallises with three molecules of water, the hydrate melting in a capillary tube at  $54.5-55^{\circ}$  ( $54.5-55^{\circ}$  corr.). It is rendered anhydrous by drying over sulphuric acid in a vacuum. The behaviour of the anhydrous salt on heating is very varied. It sometimes melts sharply at  $168^{\circ}$ , resolidifies, and melts at  $193-194^{\circ}$  ( $197-198^{\circ}$  corr.). Occasionally, the intermediate melting point is not observed at all, or is only indicated by a slight shrinking. If the anhydrous salt is dried for half an hour at  $120^{\circ}$ , only the higher melting point,  $193-194^{\circ}$ , is observed. The probable explanation is that the product, which melts at  $168^{\circ}$ , is either an amorphous form or a metastable, crystalline form of the anhydrous salt, and the transformation of one form into the other is accelerated by rise of temperature. *l-Hyoscyne hydrobromide* behaves similarly:

0.1842, dried over  $\text{H}_2\text{SO}_4$ , lost 0.0228.  $\text{H}_2\text{O}=12.38$ .

0.1813, dried at  $100^{\circ}$ , lost 0.0226.  $\text{H}_2\text{O}=12.47$ .

0.1587, ,,  $100^{\circ}$  gave 0.0778 AgBr. Br=20.85.

$\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}, \text{HBr}, 3\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}=12.33$  per cent.

$\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}, \text{HBr}$  requires Br=20.80 per cent.

The specific rotatory power of the hydrated salt was determined in water:

$c=2.842$ ;  $l=2\text{-dcm.}$ ;  $\alpha+1^{\circ}18.5'$ ;  $[\alpha]_{\text{D}}+23.02^{\circ}$ .

$c=2.525$ ;  $l=2\text{-dcm.}$ ;  $\alpha+1^{\circ}10'$ ;  $[\alpha]_{\text{D}}+23.10^{\circ}$ .

The mean of these values gives for the anhydrous salt  $[\alpha]_{\text{D}}+26.3^{\circ}$  and for the *d*-hyoscinium ion  $[\alpha]_{\text{D}}+33.2^{\circ}$ . The latter value is in approximate agreement with that calculated from the molecular rotation of the bromocamphorsulphonate (p. 502), namely,  $+30.2^{\circ}$ .

*d-Hyoscyne Aurichloride*.—*d*-Hyoscyne bromocamphorsulphonate (0.3 gram) was dissolved in 5 c.c. of warm water, and 5 c.c. of 10 per cent. hydrochloric acid were added, followed by 7 c.c. of gold chloride solution (1 in 30). The aurichloride separated, partly in isolated, minute, rectangular plates, but for the most part in fern-like growths or spangles. It melted at  $202-203^{\circ}$  and weighed 0.32 gram. It was twice recrystallised from 2.5 per cent. hydrochloric acid, the melting point each time remaining at  $204-205^{\circ}$  ( $208-209^{\circ}$  corr.) (decomp.). The recrystallised solid separated in long, flattened, orange-yellow needles with both edges serrated:

0.1266, air-dried, gave 0.0387 Au. Au=30.6.

$\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}, \text{AuCl}_3, \text{HCl}$  requires Au=30.7 per cent.

*d-Hyoschine Picrate*.—Prepared from *d*-hyoschine bromocamphorsulphonate by double decomposition in aqueous solution, this salt separated as a netted mass of needles melting and decomposing at 187—188° (see *l*-hyoschine picrate).

### *l-Hyoschine*.

*l-Hyoschine Hydrobromide*.—The properties of this salt are the same as those of *d*-hyoschine hydrobromide. The rotation of the purest hydrobromide crystallised from water was a fraction less than *d*-hyoschine hydrobromide. For various samples, the following values were obtained:

$$c = 2.454; l = 2\text{-dcm.}; \alpha = -1.07'; [\alpha]_D - 22.75^\circ.$$

$$c = 2.543; l = 2\text{-dcm.}; \alpha = -1.09.3'; [\alpha]_D - 22.71^\circ.$$

$$c = 2.045; l = 2\text{-dcm.}; \alpha = -55.43'; [\alpha]_D - 22.58^\circ.$$

The mean of the first two values gives  $[\alpha]_D - 25.93^\circ$  for the anhydrous salt, and for the *l*-hyoscinium ion  $[\alpha]_D - 32.73^\circ$ , whereas for the purest *d*-hyoschine hydrobromide the values were  $26.3^\circ$  and  $33.2^\circ$  respectively. The use of *l*- $\alpha$ -bromo- $\pi$ -camphorsulphonic acid for purifying the *l*-hyoschine would no doubt lead to complete accord between the rotatory powers of the two enantiomorphs.

*l-Hyoschine Aurichloride*.—*l*-Hyoschine hydrobromide (0.2 gram) was converted into base, using sodium hydrogen carbonate and chloroform. A solution of the hydrochloride was mixed with gold chloride solution, and the *l*-hyoschine aurichloride collected. It weighed 0.28 gram, and melted and decomposed at 204—205°. It was recrystallised from one hundred times its weight of 2.5 per cent. hydrochloric acid, and separated in complex, needle-shaped growths serrated on both edges, exactly as observed for the dextro-enantiomorph. The melting and decomposing point was unchanged (208—209° corr.):

0.1075, air-dried, gave 0.0331 Au. Au=30.8.

$C_{17}H_{21}O_4N, AuCl_3, HCl$  requires Au=30.7 per cent.

*l-Hyoschine Auribromide*.—This was prepared by Jowett's method (T., 1897, 71, 680), by dissolving 0.2 gram of *l*-hyoschine hydrobromide in excess of hydrobromic acid and adding gold chloride solution. The yield was 0.4 gram (m. p. 187—188°). It was recrystallised from boiling 2.5 per cent. hydrobromic acid (40 c.c.), and gave 0.35 gram of long, rectangular, chocolate-red leaflets still melting and decomposing at 187—188° (191—192° corr.):

0.1075, air-dried, gave 0.0258 Au. Au=24.0.

$C_{17}H_{21}O_4N, AuBr_3, HBr$  requires Au=24.0 per cent.

*l-Hyoschine Picrate*.—0.20 Gram of *l*-hyoschine hydrobromide by



double decomposition with a hot saturated picric acid solution gave 0.25 gram of *l*-hyoscine picrate crystallising in slender, primrose-yellow needles (m. p. 187—188°). It required a hundred times its weight of boiling water to dissolve it, and then separated in flat, irregular, six-sided scales covered with striations. Occasionally, these scales were united in the form of long, flat, serrated needles. It now melted and decomposed at 187.5—188.5° (191—192° corr.), and amounted to 0.2 gram.

### *dl-Hyoscine.*

*dl-Hyoscine Hydrobromide.*—Two and a-half grams each of the purest *d*-hyoscine and *l*-hyoscine hydrobromides were combined and recrystallised from water. The product crystallised exceedingly well with three molecules of water of crystallisation, and was indistinguishable from the active *d*- or *l*-hyoscine hydrobromides. The crystals were collected, and amounted to 3.3 grams. In a capillary tube, the uncrushed crystals melted at 55—58°, but powdered crystals only partly melted up to 60°, owing to rapid loss of water. The anhydrous salt melts at 181—182° (185—186° corr.). The hydrated salt effloresces on exposure to the air, in this respect differing from the active components. A 2.5 per cent. solution in water was optically inactive:

0.2217 uneffloresced salt lost 0.0274 in a vacuum.  $H_2O = 12.36$ .

0.1943, dried in a vacuum, gave 0.0949 AgBr.  $Br = 20.8$ .

$C_{17}H_{21}O_4N \cdot HBr \cdot 3H_2O$  requires  $H_2O = 12.33$  per cent.

$C_{17}H_{21}O_4N \cdot HBr$  requires  $Br = 20.8$  per cent.

*dl-Hyoscine Base.*—One gram of *dl*-hyoscine hydrobromide was converted into base, using chloroform and sodium hydrogen carbonate. The chloroform-free base was moistened with water, and when kept for some hours in a freezing mixture crystallised in minute needles. The product was collected, washed with water, and, when dried in the air, amounted to 0.55 gram. It melted at 38—40°:

0.1034, in a vacuum over  $H_2SO_4$ , lost 0.0104.  $H_2O = 10.1$ .

$C_{17}H_{21}O_4N \cdot 2H_2O$  requires  $H_2O = 10.6$  per cent.

It was recrystallised by dissolving in a little warm alcohol and adding water until a turbidity developed. On inoculation, it crystallised slowly in well-formed, transparent, chisel-shaped prisms. The melting point was unchanged at 38—40° (38—40° corr.). When dried in a vacuum over sulphuric acid, it lost two molecules of water:

0.0770 lost 0.0082.  $H_2O=10.6$ .

$C_{17}H_{21}O_4N, 2H_2O$  requires  $H_2O=10.6$  per cent.

The anhydrous material consisted of a clear varnish, and had no definite melting point.

The melting point of the dihydrate was unchanged after keeping in a Jena-glass tube for ten months.

*dl-Hyosine Picrate*.—This salt was prepared in aqueous solution by adding a saturated solution of picric acid to a solution of *dl*-hyosine hydrobromide. An oil separated at first, but was displaced, on warming, by short needles, which melted and decomposed at  $173-174^\circ$ . These were recrystallised from one hundred parts of boiling water, and separated in rosettes of long needles, melting and decomposing at  $173.5-174.5^\circ$  ( $177.5-178.5^\circ$  corr.).

The same salt is obtained from the *dl*-base.

*dl-Hyosine Aurichloride*.—This salt crystallises in long, flat needles with one edge serrated on mixing aqueous solutions of the two components. It melted and decomposed at  $214-215^\circ$ . On recrystallisation from 2.5 per cent. hydrochloric acid, it separated in stout, boat-shaped crystals melting and decomposing at  $218-219^\circ$  (corr.):

0.1175 gave 0.0358 Au. Au=30.5.

$C_{17}H_{21}O_4N, AuCl_3, HCl$  requires Au=30.7 per cent.

*dl-Hyosine Auribromide*.—On mixing *dl*-hyosine hydrobromide dissolved in excess of hydrobromic acid with gold chloride solution, this salt crystallises in chocolate-coloured leaflets of indefinite shape melting and decomposing at  $209-210^\circ$ . On recrystallisation from 50 parts of dilute hydrobromic acid solution, it separated in chocolate-red leaflets very similar in appearance to the *laevo*-salt. The melting and decomposing point was unchanged at  $213-214^\circ$  (corr.):

0.1123 gave Au=0.0268. Au=23.9.

$C_{17}H_{21}O_4N, AuBr_3, HBr$  requires Au=24.0 per cent.

Jowett (*loc. cit.*) has described a hyosine auribromide melting at  $210^\circ$ , which probably indicates that his starting material, hyosine hydrobromide, was optically inactive, or practically so.

#### *Hydrolysis of l-Hyosine.*

*With Hydrobromic Acid*.—Pure hydrated *l*-hyosine hydrobromide (1.4447 grams),  $[\alpha]_D -22.7^\circ$  ( $c=2.5$ ), was dissolved in 30 c.c. of 10 per cent. hydrobromic acid, and the rotation determined. The solution was then boiled gently under reflux, the

rotation being observed at definite intervals by cooling the solution and removing the requisite volume for the observation. On completion of the latter, the solutions were recombined and the boiling started afresh. The following data were obtained, using a 2-dcm. tube:

Initial reading .....	-141'	After 4 hours' boiling .....	-159'
After 1 hour's boiling ...	-149'	„ 6 „ „ .....	-161'
„ 2 hours' „ ...	-153'	„ 9 „ „ .....	-157'

The solution was now thoroughly extracted with purified ether to remove the *l*-tropic acid. The residual aqueous solution still showed a rotation of  $-10'$ , and contained non-hydrolysed hyoscine, as it gave a reaction with Mayer's reagent (oscine gives no reaction in acid solution of this strength). The hydrolysis was continued for a further five hours, when the rotation rose to  $-11'$ , and the reaction for hyoscine was negative. On removal of the *l*-tropic acid by ether, the residual solution was inactive.

The ethereal extracts gave 0.65 gram of crude *l*-tropic acid melting at  $125-127^{\circ}$  and having  $[\alpha]_D -70.5^{\circ}$  in water ( $c=1$ ). On recrystallisation from water, it melted at  $127-128^{\circ}$  and gave  $[\alpha]_D -76^{\circ}$  ( $c=2$ ).

The *dl*-oscine hydrobromide solution was concentrated rapidly under diminished pressure to a syrup, when it acquired a purple colour, which disappeared on dilution with water, but in absolute alcohol became brown. The syrupy residue crystallised on inoculating with *dl*-oscine hydrobromide. The crude product melted at  $270^{\circ}$  and weighed 0.75 gram (theory, 0.78). It was triturated with a little absolute alcohol, and the crystals were collected. The product consisted of granular crystals with a violet colour (probably containing traces of a perbromide (compare Schmidt, *Arch. Pharm.*, 1905, **243**, 567), weighed 0.53 gram, and melted at  $280^{\circ}$ . A mixture with pure *dl*-oscine hydrobromide (m. p.  $282^{\circ}$ ) also melted at  $280^{\circ}$ . The filtrate was now evaporated to dryness under diminished pressure, dissolved in 10 per cent. sodium hydroxide solution, and completely extracted with chloroform. On removal of the chloroform, 0.15 gram of base was obtained, which only crystallised on inoculation with the *dl*-oscine base of commerce. It melted at  $98-100^{\circ}$ , and a mixture with pure oscine melted at  $103^{\circ}$ .

The products of the hydrolysis are therefore *l*-tropic acid and *dl*-oscine.

*With Hydrochloric Acid.*—Pure *l*-hyoscine base prepared from 0.5014 gram of *l*-hyoscine hydrobromide,  $[\alpha]_D -22.75^{\circ}$ . ( $c=2.5$ ), using sodium hydrogen carbonate and chloroform, was dissolved in

30 c.c. of 10 per cent. hydrochloric acid. The rotation was followed as in the case of the hydrobromide.

Initial reading .....	-52'
After 2 hours' boiling .....	-55'; $l = 2\text{-dem.}$
" 4 " " .....	-56'
" 8 " " .....	-54.5'

On removal of the *l*-tropic acid (0.15 gram; m. p. 124—125°) by ether, the acid aqueous solution was optically inactive, and when evaporated to dryness with absolute alcohol gave 0.13 gram of *dl*-oscine hydrochloride crystallising in minute, rectangular plates, or associated together in fern-like growths. It was converted into the picrate, which crystallised in small, flattened rhombs or tablets melting and decomposing at 231°. A mixture with pure *dl*-oscine picrate, which crystallises similarly and melts and decomposes at 237—238°, melted intermediately at 232°.

In conclusion, the author desires to express his warmest thanks to Dr. Pyman for his advice and criticism throughout the course of the work.

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### XXXVIII.—*The Basic Properties of Oxygen in Organic Acids and Phenols; and the Quadrivalency of Oxygen.*

By JOSEPH KNOX and MARION BROCK RICHARDS.

OXYGEN is usually regarded as a bivalent element in most compounds, but its position in Group VI of the Periodic Table affords good ground for the assumption that it may in certain cases have a higher valency from analogy to sulphur, selenium, and tellurium, all of which may function, not only as bivalent, but also as quadrivalent and sexavalent elements.

The quadrivalency of oxygen has been assumed from time to time to explain the constitution of certain compounds, a summary of the earlier assumptions of this nature being given by Walden (*Ber.*, 1901, **34**, 4185). The work of Collie and Tickle on

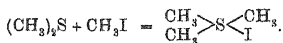
dimethylpyrone (T., 1899, **75**, 710), and of Baeyer and Villiger (*Ber.*, 1901, **34**, 2679; 1902, **35**, 1201), first drew general attention to the subject. The former were of the opinion that only in specially favourable cases could additive compounds containing quadrivalent oxygen be formed, but the latter showed that organic compounds of practically all classes containing oxygen, such as ethers, alcohols, aldehydes, ketones, etc., could combine with acids to give crystalline salts. Since that time, many similar assumptions of the quadrivalency of oxygen have been made, for example, by Bülow and Sicherer for salts of anhydrobenzopyranols and benzopyranols (*Ber.*, 1901, **34**, 3916), by Kehrmann and Mattisson for salts of phenanthraquinone (*Ber.*, 1902, **35**, 343), by Willstätter and Pummerer for compounds of pyrone with acids (*Ber.*, 1904, **37**, 3740), by Farmer for acid salts of monobasic acids (T., 1903, **83**, 1440), by Cohen and Gatecliff for compounds of ethers with nitric acid (P., 1904, **20**, 194; but see also McIntosh, *J. Amer. Chem. Soc.*, 1905, **27**, 1013), by Blaise for compounds of magnesium iodide and zinc iodide with ethers (*Compt. rend.*, 1904, **139**, 1211; 1905, **140**, 661), and by Meyer for salt-like compounds of quinones with acids (*Ber.*, 1908, **41**, 2568).

Much work on this subject has been done by McIntosh and his collaborators, who have prepared additive compounds of ethers, alcohols, aldehydes, ketones, etc., with halogens and anhydrous halogen hydrides (T., 1904, **85**, 919, 1098; 1905, **87**, 784; *J. Amer. Chem. Soc.*, 1905, **27**, 26, 1013; 1906, **28**, 588; 1908, **30**, 1097; 1910, **32**, 542, 1330; 1911, **33**, 70; 1912, **34**, 1273).

Fewer instances have been recorded of the formation of additive compounds of organic acids and phenols with other acids. Baeyer and Villiger obtained no crystalline compounds of acids with acids (*Ber.*, 1901, **34**, 2692). Hoogewerff and van Dorp, however, prepared additive products of sulphuric acid with various organic acids, and of phenols with phosphoric acid (*Rec. trav. chim.*, 1899, **18**, 211; 1902, **21**, 349). Maass and McIntosh obtained a compound of benzoic acid with hydrogen bromide, and of resorcinol with hydrogen bromide and hydrogen chloride (*J. Amer. Chem. Soc.*, 1911, **33**, 70). Pfeiffer also has prepared a number of compounds of organic acids with acids (*Ber.*, 1914, **47**, 1593), and in a recent series of papers Kendall has described the isolation, by the freezing-point method, of additive compounds of organic acids in pairs, of organic acids and phenols with sulphuric acid, and of phenols with organic acids (*J. Amer. Chem. Soc.*, 1914, **36**, 1722, 2498; 1916, **38**, 1309).

It will be seen that the organic compounds which form these

additive products are of the most diverse types. In practically all the cases cited, the organic compound is combined with an acid, forming an unstable additive compound, so that evidently the compound formation is due to basic properties in oxygen of higher valency than two. These additive compounds are generally regarded as "oxonium" compounds, containing quadrivalent oxygen, derived from the hypothetical base  $H_3O \cdot OH$ , analogous to the sulphonium compounds formed by the passage of sulphur from bivalency to quadrivalency. A typical example is Friedel's dimethyl ether hydrochloride (*Bull. Soc. chim.*, 1875, [ii], **24**, 160):  $(CH_3)_2O + HCl = \begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} O > \begin{matrix} H \\ | \\ Cl \end{matrix}$  the analogy of which to a sulphonium compound is evident:



The sulphonium salts are derivatives of the strongly basic sulphonium hydroxide,  $R_3S \cdot OH$ , so that in the salt-like character of the oxonium compounds, and the basic properties of quadrivalent oxygen, there is a parallel in the case of well-known sulphur compounds.

To explain the formation of these additive compounds, special kinds of valencies of oxygen have from time to time been assumed—crypto-valencies, complex valencies, residual affinities. In view of the fact, however, that oxygen may exhibit a higher valency than two in the ordinarily accepted sense, there seems to be no reason to assign special kinds of valencies to oxygen, any more than to sulphur or the other elements of the same group.

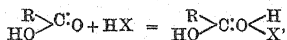
The additive products of organic oxygen compounds with acids have mainly been isolated in the solid state, and very little work has been done on the investigation of these compounds in solution. The compounds are all more or less unstable, and for the most part are decomposed by water into their original constituents. Farmer, for instance, could find no evidence for the existence of acid salts in solution (T., 1903, **83**, 1440), but there is evidence to show that oxonium compounds do exist to a certain extent, at least, in solution. Thus Maass and McIntosh (*J. Amer. Chem. Soc.*, 1913, **35**, 535), by a study of the conductivity measurements of the two component systems—hydrochloric acid and ethyl ether, hydrochloric acid and methyl ether, hydrochloric acid and ethyl alcohol, hydrochloric acid and methyl alcohol—showed the probability of the existence of the compounds in solution. Rörðam (*J. Amer. Chem. Soc.*, 1915, **37**, 557), by comparing the conductivity of a solution

of dimethylpyrone hydrochloride with that of a solution of hydrochloric acid with the same concentration of chlorine ions, electrometrically measured, proved that dimethylpyrone hydrochloride is a real salt showing electrolytic dissociation as well as hydrolytic dissociation into its components. Schuncke (*Zeitsch. physikal. Chem.*, 1894, **14**, 331) found that the solubility of ether is greater in hydrochloric acid solutions than in water, and increases with the concentration of the hydrochloric acid, and Jüttner (*Zeitsch. physikal. Chem.*, 1901, **38**, 56) gave as the reason the formation of ether hydrochloride in solution. Similarly, Sackur (*Ber.*, 1902, **35**, 1242) found that the solubility of cineole increases in hydrochloric, nitric, and acetic acid solutions.

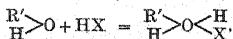
It is possible, therefore, that the existence of other oxonium compounds in solution may be shown by solubility determinations. If additive compounds of organic acids with acids exist in solution, we should expect to find some influence of this salt-formation on the solubility of the organic acid in solutions of the other acids. If no such disturbing influence comes into play, the solubility of the organic acid should continuously diminish with increasing concentration of the solvent acid, in accordance with the law that the solubility of an electrolyte is diminished by the addition of another electrolyte with a common ion.

A few instances have actually been recorded where organic acids do not obey this law. Thus, Herz (*Zeitsch. anorg. Chem.*, 1910, **66**, 93) found that for solutions of oxalic acid in boric acid the solubility increases continuously with the concentration of the boric acid. Stépanov (*Annalen*, 1910, **373**, 221) found that for picric acid in hydrochloric acid solutions the solubility diminishes to a certain point, after which it begins to increase. Masson (T., 1912, **101**, 103) found a similar result for solutions of oxalic acid in hydrochloric and nitric acid solutions.

It seems very probable that these cases may be instances of a general phenomenon, and that the unexpected results obtained for the solubility curves are caused by the existence in solution of an oxonium compound, formed by direct addition of the ions of the solvent acid to an oxygen atom of the organic acid, according to the equation



or, for phenols,



This assumption would be sufficient to account for the observed results. At first with a strong solvent acid, such as hydrochloric or nitric, the effect of the common hydrogen ion prevails, and the solubility diminishes. With increasing concentration of the solvent acid, however, the influence of the formation of the more readily soluble salt becomes stronger, and the solubility reaches a minimum, and finally begins to increase. If the solvent acid is weak, for example, boric acid, the initial decrease may be too small to be measurable; hence the only perceptible effect would be the continuous increase observed by Herz.

If the true explanation of the results observed by Herz, Stépanov, and Masson is the formation of an oxonium compound in solution, we should expect other organic acids to behave in a similar manner, and the present investigation serves to prove that this is actually the case.

## EXPERIMENTAL.

### I. *Acids.*

The solubilities of a number of organic acids of practically all classes have been determined in solutions of other acids. The number of organic acids which could be used was greatly limited by the lack of suitable methods of analysis. Many of the commonest acids could not be employed, since no sufficiently accurate method is known for their estimation, or since, even at the ordinary temperature, they volatilise from solution on evaporation. Much time was spent in testing various analytical methods given in the literature for a large number of acids, and in determining whether the acids volatilised from solution on evaporation. Amino-acids were avoided, as the presence of the basic amino-group might lead to the formation of salts of the ammonium type. In most cases, the solvent acid is hydrochloric, but experiments have also been performed in nitric, sulphuric, acetic, formic, and lactic acids.

The following series have been investigated:

*Monobasic Acids.*—Phenylacetic, diphenylacetic, benzilic, *o*-nitrobenzoic, *m*-nitrobenzoic, 3:5-dinitrobenzoic, cinnamic, diphenylene-glycollic, trichlorolactic, mandelic, diphenic, and salicylic acids in hydrochloric acid solutions; trichlorolactic acid in sulphuric acid; mandelic acid in sulphuric, acetic, and formic acids.

*Dibasic Acids.*—Malonic acid in hydrochloric and sulphuric acids; oxalic acid in sulphuric, acetic, formic, and lactic acids;



phthalic acid in hydrochloric and nitric acids; suberic acid in hydrochloric, nitric, sulphuric, and acetic acids; succinic acid in hydrochloric, nitric, sulphuric, acetic, and formic acids; and tartaric acid in hydrochloric, sulphuric, and acetic acids.

*Tribasic Acid.*—Citric acid in hydrochloric and sulphuric acids.

*Method.*—The solubilities were determined at 25°, excess of the solid being shaken for several days in a thermostat with solutions of the solvent acid of varying concentration. After saturation, the clear solution was analysed both for dissolved and solvent acid by one of the following methods:

(1) Solvent acid determined gravimetrically; dissolved acid by direct weighing after evaporation in a vacuum over soda-lime.

This method was used for most of the sparingly soluble acids in hydrochloric acid solutions.

(2) Total acidity determined by titration with standard sodium hydroxide; dissolved acid by weighing after evaporation either (a) in a vacuum, or (b) on the steam-bath; solvent acid by difference.

This method was used for nitric, acetic, and formic, and in a few cases for hydrochloric, acid solutions.

(3) Total acidity by titration; solvent acid gravimetrically; dissolved acid by difference.

Sulphuric acid solutions were analysed by this method, also cases of acids very readily soluble in hydrochloric acid.

(4) Permanganate methods for oxalic acid solutions: total acidity by alkali; oxalic acid by potassium permanganate, either (a) directly, in sulphuric acid solutions, or (b) after precipitation as calcium oxalate in other cases; solvent acid by difference.

Where an evaporation method was used, a preliminary test was made to ascertain whether the organic acid was left unchanged after evaporation from a solution in the solvent acid.

The results of the various experiments are given in the following tables. The method of analysis is indicated in each case by a number corresponding with the above arrangement, and reference is made to the diagram in which the corresponding solubility curve is to be found. In all cases, the concentrations of the acids are expressed in equivalent normalities.

(1) *Phenylacetic Acid in Hydrochloric Acid. Method 1. Fig. 1.*

HCl.....	0	1.417	2.890	4.313	5.770	7.175	8.590	9.988	11.36
C <sub>6</sub> H <sub>5</sub> O <sub>2</sub> .....	0.1310	0.0984	0.0833	0.0763	0.0739	0.0756	0.0815	0.0916	0.1099

(2) *Diphenylacetic Acid in Hydrochloric Acid. Method 2(b).*

HCl.....	0	1.620	2.913	4.512	5.973	7.349	8.889	10.27	11.74
C <sub>13</sub> H <sub>12</sub> O <sub>2</sub> .....	0.00060	0.00047	0.00040	0.00036	0.00038	0.00041	0.00042	0.00046	0.00053

(3) *Benzilic Acid in Hydrochloric Acid. Method 2(b).*

HCl.....	0	1.537	2.977	4.440	5.934	7.356	8.803	10.25	11.69
C <sub>14</sub> H <sub>12</sub> O <sub>3</sub> .....	0.00769	0.00332	0.00233	0.00182	0.00172	0.00150	0.00167	0.00195	0.00217

(4) *o-Nitrobenzoic Acid in Hydrochloric Acid.\* Method 1.*

HCl.....	0	1.314	2.607	3.909	5.013	6.509	7.795	9.080	10.30
C <sub>7</sub> H <sub>5</sub> O <sub>4</sub> N .....	0.0470	0.0280	0.0256	0.0239	0.0235	0.0233	0.0237	0.0250	0.0267

(5) *m-Nitrobenzoic Acid in Hydrochloric Acid. Method 1.*

HCl.....	0	1.416	3.310	4.308	5.953	7.044	8.380	9.793	11.54
C <sub>7</sub> H <sub>5</sub> O <sub>4</sub> N .....	0.0214	0.0175	0.0178	0.0183	0.0205	0.0225	0.0256	0.0293	0.0368

\* It may be mentioned that Kendall (*Proc. Roy. Soc.*, 1911, [A], 85, 200) gives results for the solubilities of *o*-nitrobenzoic acid, and salicylic acid, in hydrochloric acid solutions; but with the low concentrations of hydrochloric acid used in his experiments, only the decrease in solubility is observed.

## (6) 3:5-Dinitrobenzoic Acid in Hydrochloric Acid. Method 2(b).

HCl.....	0	1.565	2.908	4.594	5.657	7.336	8.855	10.27	11.73
$C_7H_4O_6N_2$ .....	0.00635	0.00398	0.00470	0.00583	0.00690	0.00841	0.00965	0.01095	0.01240

## (7) Cinnamic Acid in Hydrochloric Acid. Method 1.

HCl.....	0	2.100	4.174	6.250	8.007	10.29	10.47
$C_9H_8O_2$ .....	0.00385	0.00283	0.00272	0.00318	0.00400	0.00556	0.00572

## (8) Diphenylglycollic Acid in Hydrochloric Acid. Method 2(b).

HCl.....	0	1.952	3.907	5.843	7.745
$C_{14}H_{10}O_3$ .....	0.01082	0.00493	0.00355	0.00343	0.00332

## (9) Trichlorolactic Acid in Hydrochloric Acid. Method 3.

HCl .....	0	1.234	2.837	4.388	5.982	7.675	8.959	10.65	11.86	12.17
$C_3H_3O_3Cl_3$ .....	4.024	2.545	1.425	0.984	0.760	0.659	0.624	0.57	0.57	0.60

## (10) Trichlorolactic Acid in Sulphuric Acid. Method 3.

$H_2SO_4$ .....	0	2.525	6.166	9.588	12.75	16.28	19.38	22.28	25.34
$C_3H_3O_3Cl_3$ .....	4.024	1.896	0.671	0.353	0.26	0.16	0.18	0.21	0.26

## (11) Salicylic Acid in Hydrochloric Acid.\* Method 1.

HCl .....	0	1.459	3.057	4.374	6.164	7.311	8.730	10.20	11.54	12.20
$C_7H_6O_3$ .....	0.01613	0.00982	0.00822	0.00715	0.00654	0.00656	0.00666	0.00710	0.00794	0.00856

\* See footnote on preceding page.

(12) *Diphenic Acid in Hydrochloric Acid. Method 2(b).*

HCl .....	0	2.103	3.985	5.928	7.748
$C_6H_5O_4$ .....	0.00520	0.00182	0.00144	0.00112	0.00118

(13) *Mandelic Acid in Hydrochloric Acid. Method 1. Fig. 2.*

HCl .....	0	1.202	2.481	3.753	5.017	6.271	7.523	8.748	9.937	10.35
$C_6H_5O_3$ .....	1.191	0.691	0.488	0.387	0.332	0.307	0.302	0.316	0.353	0.375

(14) *Mandelic Acid in Sulphuric Acid. Method 3. Fig. 2.*

$H_2SO_4$ .....	0	2.695	5.390	8.294	11.05	13.62	16.50	18.89	21.17
$C_6H_5O_3$ .....	1.191	0.484	0.278	0.186	0.18	0.18	0.16	0.23	0.27

(15) *Mandelic Acid in Acetic Acid. Method 2(a). Fig. 2.*

$C_2H_3O_2$ .....	0	0.870	1.338	1.860	2.618	3.644	4.249	4.738	6.485	8.60	9.85	12.30
$C_6H_5O_3$ .....	1.191	1.808	2.312	2.664	3.186	3.444	3.472	3.487	3.509	3.234	2.996	2.178

(16) *Mandelic Acid in Formic Acid. Method 2(a). Fig. 2.*

$CH_3O_2$ .....	0	2.268	4.340	6.320	8.09	10.38	12.20	13.41	13.78
$C_6H_5O_3$ .....	1.191	1.768	2.180	2.383	2.430	2.434	2.525	2.750	3.327

(17) *Malonic Acid in Hydrochloric Acid. Method 3. Fig. 3.*

HCl .....	0	4.443	6.210	8.658	10.47	11.09	11.22
$C_3H_3O_4$ .....	15.01	7.70	5.99	4.71	4.32	4.26	4.30

(18) *Malonic Acid in Sulphuric Acid. Method 3. Fig. 3.*

$\text{H}_2\text{SO}_4$ .....	0	2.727	7.050	11.76	16.05	19.92	21.84
$\text{C}_3\text{H}_4\text{O}_4$ .....	15.01	11.44	6.79	4.07	3.01	3.20	4.55

(19) *Oxalic Acid in Sulphuric Acid. Method 4(a). Fig. 4.*

$\text{H}_2\text{SO}_4$ .....	0	2.187	4.524	6.835	9.225	13.63	15.57
$\text{C}_2\text{H}_2\text{O}_4$ .....	2.409	1.519	1.057	0.791	0.675	0.691	1.157
							1.804

(20) *Oxalic Acid in Lactic Acid. Method 4(b). Fig. 4.*

$\text{C}_3\text{H}_4\text{O}_3$ .....	0	1.337	2.718	4.051	5.357	7.647	8.709
$\text{C}_2\text{H}_2\text{O}_4$ .....	2.409	2.228	2.054	1.856	1.633	1.412	0.938
							0.832

(21) *Oxalic Acid in Formic Acid. Method 4(b). Fig. 4.*

$\text{CH}_2\text{O}_2$ .....	0	0.097	0.437	0.967	1.287	1.825	2.078	5.360	8.13	11.00	12.17	16.63	19.25	21.11
$\text{C}_2\text{H}_2\text{O}_4$ .....	2.409	2.382	2.385	2.411	2.414	2.441	2.430	2.326	2.131	1.868	1.758	1.496	1.508	2.339

(22) *Oxalic Acid in Acetic Acid. Method 4(b). Fig. 4.*

$\text{C}_2\text{H}_4\text{O}_2$ .....	0	0.135	0.321	0.923	1.361	1.844	8.563	5.721	8.005	9.864	12.55	14.03	14.21	14.83
$\text{C}_2\text{H}_2\text{O}_4$ .....	2.409	2.356	2.361	2.395	2.402	2.401	2.351	2.168	1.839	1.546	1.100	0.896	0.875	0.802

(23) *Phthalic Acid in Hydrochloric Acid. Method 1.*

$\text{HCl}$ .....	0	1.729	3.113	4.693	6.100	7.603	9.150	10.63	12.05
$\text{C}_8\text{H}_4\text{O}_4$ .....	0.0852	0.0422	0.0298	0.0216	0.0172	0.0135	0.0120	0.0128	0.0137

(24) *Phthalic Acid in Nitric Acid. Method 2(a).*

$\text{HNO}_3$ .....	0	2.077	4.077	6.718	9.027	10.40	12.60	14.42	15.99
$\text{C}_8\text{H}_6\text{O}_4$ .....	0.0852	0.0582	0.0470	0.0375	0.0331	0.0325	0.0350	0.0420	0.0577

(25) *Suberic Acid in Hydrochloric Acid. Method 1. Fig. 1.*

$\text{HCl}$ .....	0	1.423	2.858	4.281	5.691	7.130	8.378	9.865	11.20
$\text{C}_8\text{H}_{14}\text{O}_4$ .....	0.0680	0.0498	0.0428	0.0412	0.0432	0.0504	0.0633	0.0905	0.1370

(26) *Suberic Acid in Nitric Acid. Method 2(a).*

$\text{HNO}_3$ .....	0	0.307	0.555	0.906	1.543	2.021	4.035	5.749	8.091	10.05	11.77	13.30
$\text{C}_8\text{H}_{14}\text{O}_4$ .....	0.0680	0.0594	0.0590	0.0634	0.0695	0.0839	0.0999	0.1133	0.1575	0.2231	0.3896	0.6049

(27) *Suberic Acid in Sulphuric Acid. Method 3.*

$\text{H}_2\text{SO}_4$ .....	0	1.858	5.233	7.524	11.33	18.65
$\text{C}_8\text{H}_{14}\text{O}_4$ .....	0.068	0.039	0.037	0.042	0.06	0.20

(28) *Suberic Acid in Acetic Acid. Method 2(a).*

$\text{C}_2\text{H}_4\text{O}_2$ .....	0	0.435	0.887	2.112	4.262	6.350	8.402
$\text{C}_8\text{H}_{14}\text{O}_4$ .....	0.0680	0.0776	0.0902	0.1340	0.2891	0.4317	0.5846

(29) *Succinic Acid in Hydrochloric Acid. Method 1. Fig. 5.*

$\text{HCl}$ .....	0	2.751	5.964	7.335	8.950	10.40	11.98
$\text{C}_4\text{H}_6\text{O}_4$ .....	1.352	0.681	0.402	0.353	0.333	0.328	0.378

(30) *Succinic Acid in Nitric Acid. Method 2(a). Fig. 5.*

$\text{HNO}_3$ .....	0	1.299	3.034	5.236	6.616	9.710	11.11	13.51	15.43
$\text{C}_4\text{H}_6\text{O}_4$ .....	1.352	1.134	0.941	0.724	0.652	0.528	0.518	0.561	0.731

(31) *Succinic Acid in Sulphuric Acid. Method 3. Fig. 5.*

$\text{H}_2\text{SO}_4$ .....	0	1.981	3.816	4.926	8.122	10.22	13.81	17.05	23.18
$\text{C}_4\text{H}_6\text{O}_4$ .....	1.352	0.908	0.683	0.563	0.388	0.34	0.30	0.39	0.99

(32) *Succinic Acid in Acetic Acid. Method 2(a). Fig. 5.*

$\text{C}_4\text{H}_6\text{O}_2$ .....	0	0.078	0.448	0.916	2.828	4.536	6.655	8.661	10.34
$\text{C}_4\text{H}_6\text{O}_4$ .....	1.352	1.384	1.415	1.452	1.592	1.643	1.639	1.519	1.357
								12.40	14.64
								1.097	0.797
									16.85
									0.514

(33) *Succinic Acid in Formic Acid. Method 2(a). Fig. 5.*

$\text{CH}_3\text{O}_2$ .....	0	0.090	0.446	0.930	3.730	5.547	7.500	11.29	15.29
$\text{C}_4\text{H}_6\text{O}_4$ .....	1.352	1.369	1.397	1.408	1.501	1.531	1.449	1.228	0.944
								19.16	20.53
								0.715	0.667
									22.93
									0.604

(34) *Tartaric Acid in Hydrochloric Acid. Method 3. Fig. 6.*

$\text{HCl}$ .....	0	1.257	2.568	4.466	6.303	8.144	9.890	10.51	11.17
$\text{C}_4\text{H}_6\text{O}_6$ .....	10.26	8.528	7.092	5.434	4.35	3.77	3.43	3.42	3.42

(35) *Tartaric Acid in Sulphuric Acid. Method 3. Fig. 6.*

$\text{H}_2\text{SO}_4$ .....	0	1.798	4.043	6.807	9.895	12.54	15.46	18.10	19.85	22.17
$\text{C}_4\text{H}_6\text{O}_6$ .....	10.26	8.51	6.64	4.73	3.18	2.43	1.95	1.77	1.86	2.74

(36) *Tartaric Acid in Acetic Acid. Method 2(a). Fig. 6.*

$\text{C}_2\text{H}_4\text{O}_2$ .....	0	0.25	0.60	1.23	2.63	4.24	6.12	8.30	10.89	14.14	16.92
$\text{C}_4\text{H}_6\text{O}_6$ .....	10.26	10.09	9.875	9.515	8.717	7.718	6.548	5.151	3.505	1.594	9.344

(37) *Citric Acid in Hydrochloric Acid. Method 3.*

$\text{HCl}$ .....	0	0.949	2.189	3.795	5.718	7.736	9.635	10.36	11.09
$\text{C}_6\text{H}_8\text{O}_7$ .....	12.54	11.03	9.30	7.36	5.38	4.09	3.46	3.35	3.29

(38) *Citric Acid in Sulphuric Acid. Method 3.*

$\text{H}_2\text{SO}_4$ .....	0	1.689	4.206	7.145	10.83	11.46	14.24	18.18	20.59	22.37
$\text{C}_6\text{H}_8\text{O}_7$ .....	12.54	10.57	7.97	5.61	3.28	3.07	2.23	1.76	2.00	2.88

(39) *p-Nitrophenol in Hydrochloric Acid. Method 5(a). Fig. 7.*

$\text{HCl}$ .....	0	1.650	3.277	4.993	6.552	8.196	9.817	11.29
$\text{C}_6\text{H}_5\text{O}_3\text{N}$ .....	0.1097	0.0962	0.0913	0.0934	0.0990	0.1093	0.1230	0.1421



(40) *m*-Nitrophenol in Hydrochloric Acid. Method 5(a). Fig. 7.

HCl .....	0	1.925	3.822	5.720	7.550	9.213	10.96	11.20
C <sub>6</sub> H <sub>5</sub> O <sub>2</sub> N .....	0.0974*	0.0849	0.0834	0.0885	0.1009	0.1130	0.1284	0.1307

(41) *Picric Acid* in Nitric Acid. Method 5(b).

HNO <sub>3</sub> .....	0	1.022	2.059	4.161	6.289	8.334	10.47	12.47
C <sub>6</sub> H <sub>3</sub> O <sub>7</sub> N <sub>3</sub> .....	0.0578	0.0108	0.0124	0.0237	0.0405	0.0612	0.1006	0.1763

(42)  $\beta$ -Naphthol in Hydrochloric Acid. Method 5(a).

HCl .....	0	1.466	2.952	4.343	5.785	7.122	8.674	11.47
C <sub>10</sub> H <sub>8</sub> O .....	0.00524	0.00410	0.00360	0.00333	0.00319	0.00316	0.00307	0.00341

(43) *Resorcinol* in Hydrochloric Acid. Method 5(a).

HCl .....	0	0.656	1.671	3.410	4.402	6.076	7.567	9.157
C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> .....	6.515	5.705	4.570	3.020	2.307	1.616	1.287	1.125

\* It may be remarked that the value found for the solubility of *m*-nitrophenol in water differs considerably from that given by Vaubel (*J. pr. Chem.*, 1895, [ii], 52, 73), but as no definite particulars are given of the method employed, or of the source of his result, it cannot be regarded as very trustworthy. The compound used in the present case, which was prepared from *m*-nitroaniline, was recrystallised from water, and melted at 96–97°.

(44) *Quinol in Hydrochloric Acid. Method 5(a).*

HCl .....	0	1.892	3.793	5.729	7.597	9.237	10.97
$C_6H_5O_3$ .....	0.066	0.402	0.282	0.215	0.188	0.178	0.166

(45) *Catechol\* in Hydrochloric Acid. Method 5(a).*

HCl .....	0	1.68	3.53	5.39	7.30	9.11	10.83
$C_6H_5O_3$ .....	4.19	2.13	1.18	0.81	0.62	0.55	0.55

(46) *Styphnic Acid in Hydrochloric Acid. Method 5(b).*

HCl .....	0	1.410	2.814	4.221	5.634	6.997	8.418	11.10	11.16
$C_6H_3O_3N_3$ .....	0.02179	0.00062	0.00060	0.00072	0.00093	0.00163	0.00197	0.00379	0.00387

(47) *Styphnic Acid in Nitric Acid. Method 6(a).*

$HNO_3$ .....	0	1.785	4.171	6.234	8.368	10.31	11.97	13.97	15.57
$C_6H_3O_3N_3$ .....	0.02179	0.001403	0.002180	0.003274	0.005108	0.007944	0.01298	0.02742	0.05611

(48) *Pyrogallol in Hydrochloric Acid. Method 5(a).*

HCl .....	0	1.53	3.18	5.12	6.86	8.68	10.43	10.48
$C_6H_5O_3$ .....	4.02	2.81	1.86	1.25	1.01	0.91	0.92	0.93

\* The preliminary test showed that catechol is very slightly volatile at the ordinary temperature in a vacuum, but the regularity of the curve obtained seems to show that in spite of this the results are fairly accurate.

II. *Phenols.*

The solubility of a number of phenols has been determined in the same way, the series investigated being:

*Monohydric Phenols.*—*p*-Nitrophenol, *m*-nitrophenol, and  $\beta$ -naphthol in hydrochloric acid; trinitrophenol (picric acid) in nitric acid.

*Dihydric Phenols.*—Resorcinol, quinol, catechol, and trinitroresorcinol (styphnic acid) in hydrochloric acid; trinitroresorcinol in nitric acid.

*Trihydric Phenol.*—Pyrogallol in hydrochloric acid.

*Methods of Analysis.*—5. For all phenols in hydrochloric acid, the acid was determined gravimetrically, and the phenol by weighing after evaporation (*a*) in a vacuum, or (*b*) on the steam-bath.

6. For picric acid and styphnic acid in nitric acid, the concentrations of the nitric acid solutions were determined at 25° before adding the solid, owing to the difficulty of titrating solutions containing these phenols. As the phenols are only sparingly soluble, however, any change in volume that might occur when they dissolve could have no appreciable effect on the results. The phenol was determined by weighing, after evaporation (*a*) in a vacuum, or (*b*) on the steam-bath.

Some of the phenols gave deeply coloured solutions, but the residues obtained on evaporation were practically colourless, and a preliminary experiment showed that they were left unchanged when evaporated to dryness with hydrochloric acid or nitric acid.

The results are given in tables 39 to 48, the solubilities of the phenols being given in gram-molecules per litre, whilst the concentrations of the solvent acid are expressed, as before, in equivalent normalities.

*Consideration of Results.*

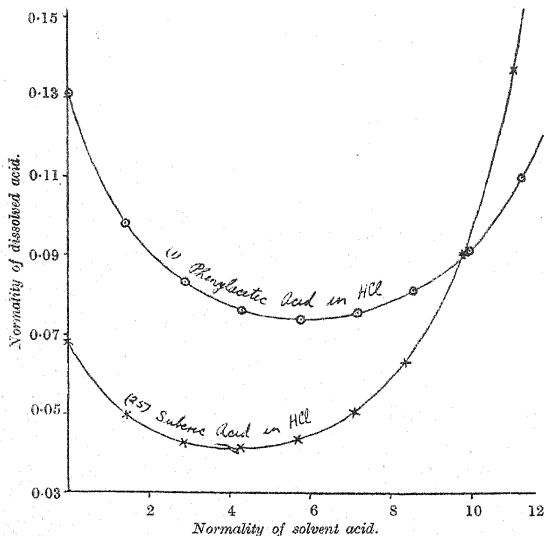
A glance at the solubility curves will suffice to show that the results observed by Herz, Stépanov, and Masson were no isolated phenomena, but that, as regards the solubility of organic acids and phenols in solutions of other acids, deviation from Nernst's law is the rule and not the exception. It will be seen that the curves obtained are of two main types, according as the solvent acid is a mineral or an organic acid, but in each case the assumption of oxonium salt-formation is sufficient to account for the observed results.

Owing to exigencies of space, only a few typical solubility curves can be reproduced. The other solubility curves, which can be

constructed from the tables, will be referred to by the number of the table containing the necessary data. Thus (1) refers to the solubility of phenylacetic acid in hydrochloric acid, and so on.

The curves obtained for solutions in the mineral acids all resemble more or less those obtained by Stépanov and Masson, that is, the solubility diminishes rapidly at first, reaches a minimum, and afterwards increases steadily with increasing concentration of the solvent acid. The results, however, vary somewhat according

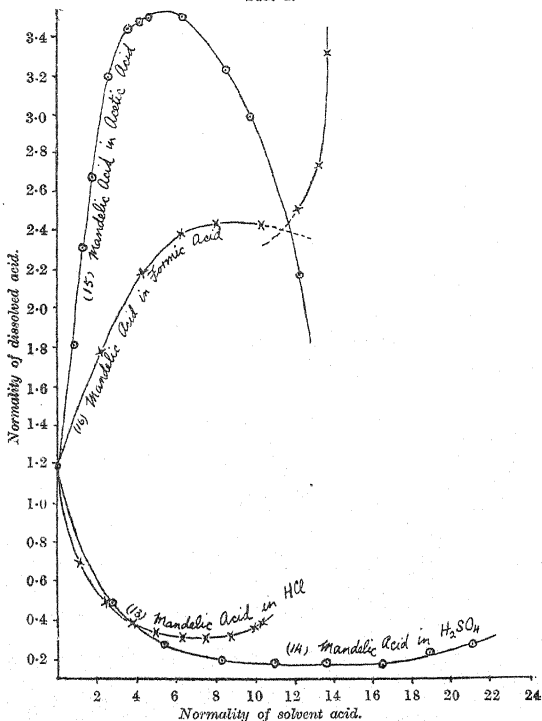
FIG. 1.



to the solubility of the organic acid or phenol, and the concentrations attainable with the mineral acid. Thus with sparingly soluble acids and phenols, such as phenylacetic (1, 25, Fig. 1) and nitrobenzoic acids (4, 5), and the nitrophenols (39, 40, Fig. 7), the curve in every case shows a distinct turning point. Other examples are 2, 3, 6, 7, 8, 11, 12, 23, 24, 25, 26, 27, 39, 40, 41, 42, 46, 47. With very readily soluble substances, such as malonic, citric, and tartaric acids, quinol, and catechol (17, Fig. 3), (34,

Fig. 6), (37, 43, 44, 45, 48), the concentration of hydrochloric acid reached is not sufficient to show clearly the upward tendency of the curve, although the general shape makes it evident that the

FIG. 2.

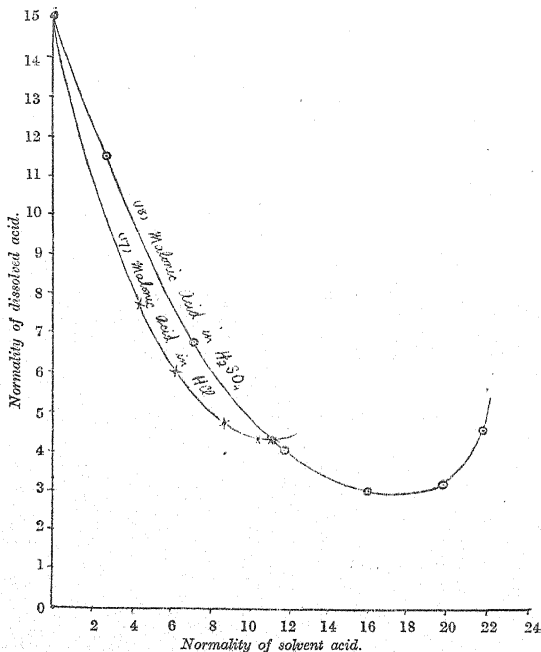


curve has reached its minimum at the concentration attained, and is just about to turn upwards—a conclusion which is further justified by the fact that in sulphuric acid solutions, where the concentrations attainable are considerably greater, even the very

readily soluble acids give a definite turning point (18, Fig. 3), (35, Fig. 6), (38).

When the solvent acid is organic, modification of the shape of the curve results from two causes, namely, (a) the weakness of organic acids in general, and (b) the wide difference between the

FIG. 3.



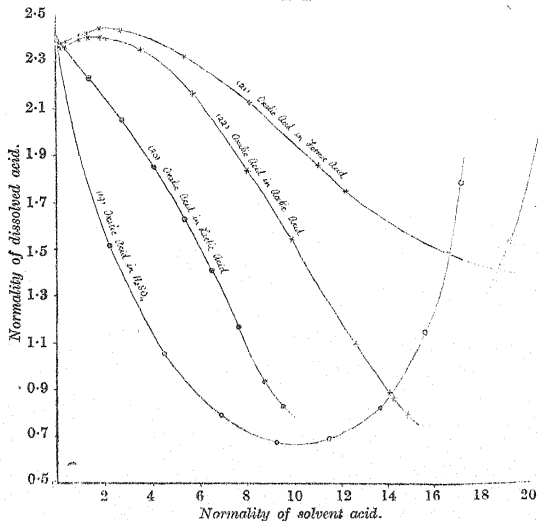
solubilities of the dissolved acid in water and in the organic acid solvent.

(a) When both solvent and dissolved acids are weak, the effect of the common hydrogen ion is, as a rule, too small to be measured. Of the acids the solubilities of which were determined in an organic acid solution, oxalic acid is the only one of sufficient acidic strength

to show any perceptible initial decrease in solubility (21, 22, Fig. 4). The others show increase in solubility from the beginning, except tartaric in acetic (36, Fig. 6), and oxalic in lactic acid (20, Fig. 4), where no evidence of salt-formation was obtained.

(b) If the dissolved acid is more readily soluble in the solvent organic acid than in water, the resulting curve shows a continuous increase—an increase which may be partly due to salt-formation or entirely due to increasing solubility in the solvent acid, so that

FIG. 4.

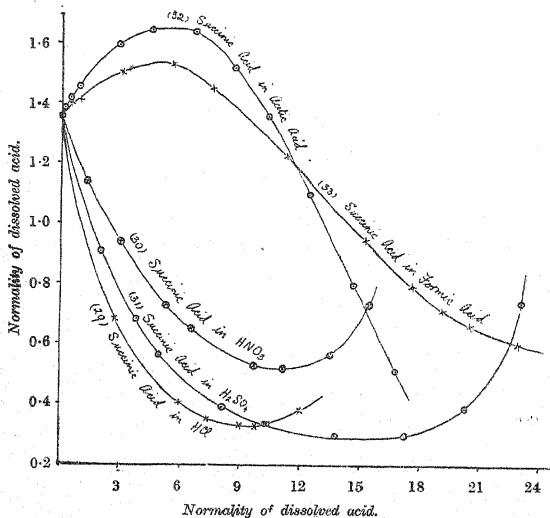


no conclusion as to salt-formation can be drawn. An instance of this may be seen in the curve for suberic acid in acetic acid (28). Other cases give clear evidence of salt-formation, the curve showing an initial increase in solubility, owing to the formation of the more readily soluble salt, with a subsequent decrease, caused by decreasing solubility in the solvent acid. The curves which show this effect clearly are: (1) succinic acid in acetic and formic acids (32, 33, Fig. 5), (2) oxalic acid in acetic and formic acids (here the ionic effect is first perceptible, before the increase due to salt-

formation) (21, 22, Fig. 4), and (3) mandelic acid in acetic and formic acids (15, 16, Fig. 2).

(It will be observed that in three of these cases, namely, oxalic acid in acetic and formic acid solutions, and mandelic acid in formic acid, there is apparently a break in the curve. The cause of this has not been investigated, but Masson, who obtained a similar break for oxalic acid in nitric acid, attributed the result to dehydration of the oxalic acid.)

FIG. 5.



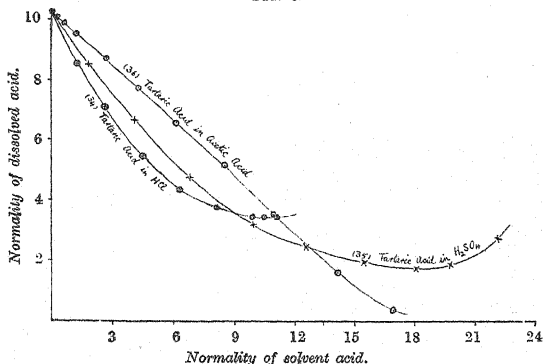
From the curves, it may be inferred that salt-formation does not take place with equal readiness in all the mineral acids. Where curves have been determined for the same organic acid or phenol both in hydrochloric and nitric acid solutions, it will be seen that in each case the nitric acid curve lies above that for hydrochloric acid, evidently indicating that additive compounds are formed more readily with nitric acid; see, for example, the curves for succinic (29, 30, Fig. 5), phthalic (23, 24), suberic (25, 26), and



styphnic acids (46, 47) in hydrochloric and nitric acid respectively.

Again, a comparison of the curves for the same acid in hydrochloric and sulphuric acid solutions shows uniformity of behaviour in all the cases investigated. There is at first a more rapid decrease in solubility in hydrochloric than in sulphuric acid (probably due to the greater acidic strength of hydrochloric acid, and the correspondingly greater ionic effect), but the turning point is more quickly reached and the hydrochloric acid curve soon cuts the other, from which we may infer that salt-formation takes place with greater ease in hydrochloric acid. A comparison of the curves for succinic (29, 31, Fig. 5), citric (37, 38), tartaric (34, 35, Fig. 6),

FIG. 6.

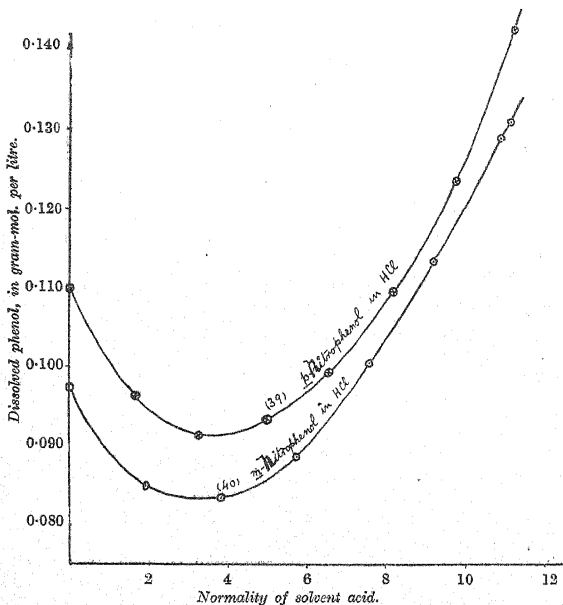


malonic (17, 18, Fig. 3), mandelic (13, 14, Fig. 2), and trichlorolactic acids (9, 10) in hydrochloric and sulphuric acids, respectively, will make this clear. (In the case of suberic acid [25, 27], the result appears to be similar, but owing to the small solubility of suberic acid, and the necessity for estimating the suberic acid in sulphuric acid solutions by difference, this curve is not sufficiently accurate to enable the distinction between the two curves to be clearly seen.) It would therefore appear that, of the mineral acids, sulphuric acid shows the least tendency to salt-formation, whilst nitric acid shows the greatest.

No quantitative connexion can be established between the turning point of the curve and the strength of the organic acid in

question. Kendall found that, in general, for additive compounds, both of organic acids in pairs and of organic acids with sulphuric acid, the tendency towards the formation of additive compounds is dependent on the difference in acidic strengths. Very weak organic acids most readily form additive compounds, and an

FIG. 7.



increase in the acidic strength is accompanied by a diminution or loss of this property. The rule is, however, merely qualitative. This result is, in general, confirmed by the present investigation, although the question is complicated by the fact that the turning point in the solubility curve depends largely on the solubility of the organic acid.

### General Summary of Results.

From determinations of the solubility of organic acids and phenols in solutions of other acids, it has been shown that in such solutions compounds are formed between the organic acid or phenol and the solvent acid. The most probable explanation is that the organic acids and phenols contain a basic oxygen atom, and that this forms salts of the oxonium type with the solvent acid, the oxygen becoming quadrivalent. This view is strongly supported by the work of Kendall, whose earlier papers were published during the progress of the present research.\*

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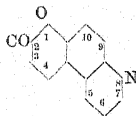
### XXXIX.— $\psi$ -1 : 8-isoNaphthoxazones.

By BIMAN BIHARI DEY and MAHENDRA NATH GOSWAMI.

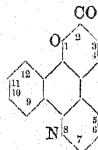
By the fusion of a pyridine with a benzene nucleus, the condensed quinoline ring is formed, and in a similar manner it is conceivable that the coumarin ring would give rise to a class of derivatives which might be represented as  $\psi$ - $\beta$ -naphthoxazones,† their relation-

\* Kendall has since published other papers on the same subject, reference to which will be found in the concluding paper of the series (*J. Amer. Chem. Soc.*, 1917, 39, 2303), in which he sums up the results of his investigations. The above research was completed early in 1916, but for various reasons publication of the results has been delayed.

† As the compounds described in this paper do not contain the true oxazine ring, they are regarded as being derived from  $\psi$ -naphthoxazines, thus :

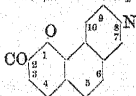


$\psi$ -1 : 8-isoNaphthoxazone.

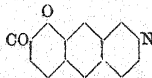


$\psi$ -Benzo-1 : 8-isonaphthoxazone.

Isomerides of  $\psi$ -1 : 8-isonaphthoxazone will thus receive the name :



$\psi$ -1 : 8- $\alpha$ -Naphthoxazone.

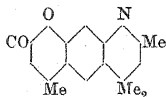


$\psi$ -1 : 8- $\beta$ -Naphthoxazone.

ship to coumarins being analogous to that of quinoline to benzene:



Substances of the latter class, so far as it has been possible to ascertain, are practically unknown, only one instance being encountered in the literature where a compound probably belonging to this category has been mentioned (Pechmann and Schwarz, *Ber.*, 1899, **32**, 3701). This substance was obtained as a by-product in the condensation of *m*-aminophenol and ethyl acetoacetate, where, in addition to the expected 7-amino-4-methylcoumarin, a small amount of a solid (m. p. 268°) was isolated, which was regarded as a dihydroquinocoumarin, and assigned the following structure:



The evidence adduced in favour of its constitution is not complete, and no further work appears to have been carried out on the subject.

The reactions which are of general applicability in the synthesis of quinoline and its allies, namely, the Skraup, the Doebner-Miller, and the Knorr reactions, are all based on the condensations of aniline or other primary aromatic amines; the same methods, with slight modifications, have now been applied to the synthesis of the  $\psi$ -naphthoxazones from the aminocoumarins and the aminonaphthacoumarins, in which the amino-groups are attached to the benzene nucleus. These compounds have been shown by previous investigators to resemble the aromatic amines in their chemical behaviour, and they may readily be diazotised and reduced to the corresponding coumarylhydrazines, etc. (Morgan and Micklethwait, *T.*, 1904, **85**, 1233; Clayton, *P.*, 1911, **27**, 246).

These considerations led to the present investigation, a systematic study of this new class of substances being also considered desirable in view of certain questions that arose with regard to the connexion between their structure and physiological properties.

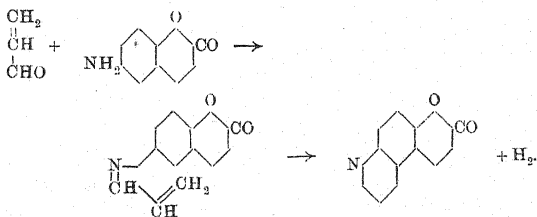
The present communication deals with the application of the Skraup synthesis to the preparation of the  $\psi$ -naphthoxazones, the

results obtained with the other reactions being incomplete and reserved for a future communication.

The Skraup reaction, which depends on the condensation of aromatic amines with glycerol and sulphuric acid in the presence of an oxidising agent, is apt to be rather violent when applied to the aminocoumarins, and it was found that the success of the operation depended to a great extent on the careful regulation of the temperature at the commencement of the reaction. It was also observed that, instead of using a mixture of nitro- and aminocoumarins, as is generally done in these reactions, the nitrocoumarins could be employed alone, without diminishing the yield of the  $\psi$ -naphthoxazones to any appreciable extent.

This observation greatly simplified the process of this synthesis, as the aminocoumarins were sometimes rather difficult to prepare from the corresponding nitro-compounds.

On treating 6-nitrocoumarin with allyl alcohol, it was reduced to the amino-compound (compare Brunner and Chuard, *Ber.*, 1885, 18, 447), and it may therefore be legitimately assumed that allyl alcohol is formed in one of the stages in the condensation and is then oxidised to the corresponding aldehyde by the nitro-compound, which is reduced in the process. The amino-compound now serves to combine with the acraldehyde, after which the reaction takes the usual course:



In their chemical characteristics, the  $\psi$ -naphthoxazones do not differ materially from the quinolines, except in their behaviour towards hot alkali hydroxides, which dissolve these substances with a deep colour. This is evidently due to the hydrolysis of the pyrone ring, and the solution presumably contains an unstable acid; on carefully neutralising the alkaline solution in the cold, the original substance is slowly deposited in the crystalline state.

The  $\psi$ -naphthoxazones, as tertiary bases, readily form salts, a large variety of the double salts having been prepared in the course of this investigation; amongst these, the dichromates, the

ferrocyanides, and the double potassium mercuri-iodides are very characteristic and form crystals having a definite structure. They also give characteristic precipitates with the general alkaloidal reagents: Wagner's solution gives a deep orange-brown, crystalline precipitate of the iodide, Scheibler's reagent gives a white, crystalline precipitate of the phosphotungstates, and Soumenschein's reagent gives a curdy precipitate of the corresponding phosphomolybdate.

Like the tertiary amines, they also unite with alkyl haloids in molecular proportions. A feature of some interest which has arisen from a study of these *N*-alkyl iodides is the remarkable phenomenon of colour exhibited by members of the series in the solid state and in solution. Although the  $\psi$ -naphthoxazones are generally colourless, and form colourless solutions in dilute mineral acids, their additive products with the alkyl iodides possess a deep colour varying in shade from dark yellow to scarlet-red. The aqueous solutions of these iodides, however, which are strongly ionised, are practically colourless.

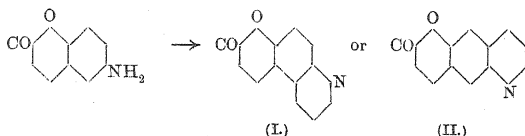
In seeking an explanation for this behaviour, the influence of ionisation, and also, perhaps, that of the alkyl group and the halogen, has to be taken into account, and it seems feasible, therefore, to suggest that the ions, basic and acidic, are colourless, whilst the undissociated molecule of the *N*-alkyl iodide is intensely coloured.

If, moreover, this interpretation is correct, it would be reasonable to expect that the solutions of these iodides in non-ionising media would be coloured. This has been observed to be the case, for although the ordinary non-ionising solvents, like benzene, chloroform, etc., were found to have little or no solvent action on these iodides, the latter dissolved in warm toluene or xylene, the solutions being generally purple with an intense pink fluorescence.

In the reduction of the  $\psi$ -naphthoxazones, the pyridine ring is first hydrogenised. The *N*-tetrahydro- $\psi$ -naphthoxazones crystallise in golden-yellow needles, and their chemical behaviour coincides exactly with that of the fatty, aromatic secondary amines; the presence of the imino-group in their molecules is shown by the characteristic nitroso- and acyl derivatives which they form with nitrous acid, acetic anhydride, etc.

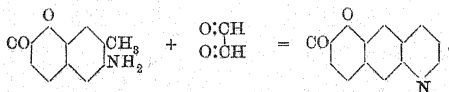
The problem of ascertaining the constitution of the  $\psi$ -naphthoxazones has been greatly simplified by a consideration of the nature of the reactions employed in their synthesis. The occurrence of the pyridine ring in the molecule has been placed beyond doubt by the isolation of quinoline by the distillation of the unsubstituted  $\psi$ -naphthoxazone with zinc dust. The next question

of importance that has to be settled in order to arrive at a definite structure for each individual member of the series concerns the manner of attachment of the pyridine to the benzene nucleus. Thus, the reaction by which  $\psi$ -1:8-naphthoxazone is synthesised from 6-aminocoumarin may follow two different courses, according as the carbon atom adjacent to the amino-group taking part in the condensation occupies position 5 or 7 in the benzene ring. The compound in question may therefore be assigned either of the two following structures:



Although any direct evidence which might enable a decision to be made between these two possible constitutions is still lacking, the formula I appears to be the more plausible, and is also in harmony with certain general observations regarding the process of this condensation. Thus the substitution of a methyl group in position 7 does not hinder the progress of this reaction to the slightest extent, and this behaviour would be difficult to explain if it were assumed that the pyridine ring attached itself in the first place to the 7-carbon atom. The synthesis of alizarin-blue is another example of a similar nature where the condensation takes place smoothly with the *peri*-carbon atom corresponding with the 5-position in the coumarin ring.

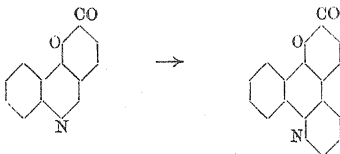
The best solution of the problem appeared to lie in the synthesis of a  $\psi$ -naphthoxazone of structure II from 6-amino-7-methylcoumarin and glyoxal, which, in the presence of alkalis, were expected to condense in the following manner (compare Kulisch, *Monatsh.*, 1895, 15, 277):



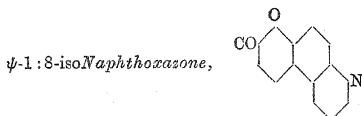
Attempts in this direction, however, have hitherto been unfruitful, and further experiments are in progress.

The determination of the structures of the  $\psi$ -benzoisonaphthoxazones which have been obtained by analogous reactions from 6-nitro- and 6-amino-1:2- $\alpha$ -naphthopyrones does not present much difficulty, as in these cases only the carbon atom 5 is free to

participate in the reaction, which can therefore proceed only in the following way:



#### EXPERIMENTAL.



This substance was first prepared from 6-aminocoumarin by heating it with glycerol and sulphuric acid in the presence of 6-nitrocoumarin as the oxidising agent, according to the original directions of Skraup (*Monatsh.*, 1880, 1, 316). The use of aminocoumarin was dispensed with later and the nitro-compound employed alone, the following conditions being found to give the most satisfactory results.

6-Nitrocoumarin (16 grams) and glycerol (19 c.c.) were mixed together, and concentrated sulphuric acid (17 grams) was gradually added, the mixture being cautiously heated in an oil-bath. A violent reaction set in at 145—150°, and as soon as this occurred the flask was removed from the bath and shaken vigorously. After the first reaction had subsided, the contents, which had now assumed a dark, tarry appearance, were again gradually heated to 160—170°, and maintained at this temperature for five to six hours. After cooling, the solid mass was broken up and repeatedly warmed with small amounts of water, and filtered until the filtrate ceased to exhibit a blue fluorescence. The latter, on keeping, deposited a small amount of crystals, which were found to be unchanged nitrocoumarin. This was removed and the acid filtrate rendered alkaline with dilute sodium hydroxide, care being taken to avoid an excess, as the freshly precipitated  $\psi$ -1:8-isonaphthoxazone dissolves to a considerable extent in dilute alkali hydroxide even in the cold. The voluminous, pale yellow precipitate was collected, washed with cold water, and crystallised twice from boiling dilute alcohol with the aid of animal charcoal.



Thin, silky needles were deposited having a faint yellow colour and melting at  $232^{\circ}$  (uncorr.). The yield of the crystallised substance amounted to a little more than 6 grams, approximating to 40 per cent. of that required by theory:

0.0930 gave 0.2488  $\text{CO}_2$  and 0.0326  $\text{H}_2\text{O}$ .  $\text{C}=72.9$ ;  $\text{H}=3.9$ .

0.1333 „ 8.3 c.c.  $\text{N}_2$  at  $30^{\circ}$  and 745 mm.  $\text{N}=6.9$ .

$\text{C}_{12}\text{H}_7\text{O}_2\text{N}$  requires  $\text{C}=73.1$ ;  $\text{H}=3.5$ ;  $\text{N}=7.1$  per cent.

The substance dissolves readily in alcohol, ether, chloroform, etc., to form colourless solutions, but its solutions in dilute sulphuric and hydrochloric acids exhibit a pale blue fluorescence, which is best seen on dilution. The crystallised substance is insoluble in dilute sodium hydroxide solution in the cold, but dissolves on boiling to give a deep yellow solution. The latter, on cooling and carefully neutralising with dilute sulphuric acid, slowly deposits the original material in a crystalline condition.

The *hydrochloride* is precipitated on passing dry hydrogen chloride into a solution of the substance in 90 per cent. alcohol. It forms a white, granular powder after being washed with absolute alcohol.

The *mercurichloride* crystallises from water in long, colourless, soft needles.

The *potassium mercuri-iodide*, which is first obtained as a curdy, white precipitate on adding Meyer's solution, very quickly changes into lustrous, leafy crystals.

The *picrate* is precipitated on mixing the constituents in hot benzene solution. It forms a yellow, crystalline powder melting at  $212^{\circ}$ .

The *platinichloride*, prepared by the usual method, crystallises in yellowish-brown needles:

0.0757 gave 0.0177 Pt.  $\text{Pt}=23.4$ .

$(\text{C}_{12}\text{H}_7\text{O}_2\text{N})_2\text{H}_2\text{PtCl}_6\text{H}_2\text{O}$  requires  $\text{Pt}=23.6$  per cent.

The *aurichloride* forms a bright yellow, crystalline precipitate, which rapidly turns brown in the air.

The *dichromate* crystallises in orange-red prisms, which are almost insoluble in water.

The *ferrocyanide* forms a shining, crystalline powder, which has a very characteristic colour resembling that of catechu. It dissolves in boiling water, the solution having an intense blue fluorescence. The ferrocyanide appears to be partly decomposed in the process of boiling its solution, as, on cooling the aqueous solution, the salt does not crystallise out, but a deep blue powder is gradually deposited along with clusters of small, colourless needles, which were identified as those of the original base.

A series of ammonium iodides has been obtained from  $\psi$ -1:8-isonaphthoxazone by union with the alkyl iodides. These were prepared by the general method of heating the base with the alkyl iodide, with the addition of a little absolute alcohol, at  $140^{\circ}$  in sealed tubes. They possess a dark yellow to red colour, are fairly readily soluble in water, and crystallise on concentrating their aqueous solutions. The following have been prepared:

$\psi$ -1:8-isonaphthoxazone N-methiodide crystallises in thin, scarlet-red plates melting at  $246^{\circ}$ . The aqueous solution has a faint yellow colour:

0.1655 gave 0.1138 AgI.  $I=37.15$ .

$C_{13}H_{10}O_2NI$  requires  $I=37.46$  per cent.

It is practically insoluble in the ordinary organic solvents, such as benzene, ether, chloroform, etc., but readily dissolves in warm xylene to form a dark red solution with a fine violet fluorescence.

The N-ethiodide,  $C_{14}H_{12}O_2NI$ , forms orange-red crystals melting at  $206^{\circ}$ . Its solution in xylene has a reddish-violet colour and exhibits an intense pink fluorescence.

The N-n-butyl iodide,  $C_{16}H_{16}O_2NI$ , forms a dark yellow powder melting and decomposing at  $209^{\circ}$ . It agrees with the foregoing derivatives in its general behaviour.

The N-amyl iodide,  $C_{17}H_{18}O_2NI$ , melts and decomposes at  $210^{\circ}$ . It closely resembles the butyl derivative in its physical properties.

In order to examine the effect of the displacement of the alkyl groups by other complex groups on the colour of these substances, the following compounds were prepared, the first two of which were practically colourless, whilst the last had a pale yellow tint.

The N-allyl bromide,  $C_{15}H_{12}O_2NBr$ , forms small, white needles melting and decomposing at  $320^{\circ}$ .

The N-benzyl chloride,  $C_{19}H_{14}O_2NCl$ , crystallises from water in green needles melting at  $265^{\circ}$ .

The N-phenylacetyl bromide,  $C_{20}H_{14}O_3NBr$ , forms a pale yellow, crystalline powder melting and decomposing at  $350^{\circ}$ .

#### 5:6:7:8-Tetrahydro- $\psi$ -1:8-isonaphthoxazone.

$\psi$ -1:8-isonaphthoxazone (2 grams) was dissolved in concentrated hydrochloric acid (30 c.c.), granulated tin (5 grams) added, and the mixture gently boiled on a sand-bath under reflux for seven to eight hours. Next day water was added, and the tin was removed as sulphide. The filtrate was concentrated to about 100 c.c., and rendered alkaline with dilute ammonia; on cooling, the tetrahydro-derivative slowly separated in golden-yellow needles.

A single crystallisation from hot water, in which it was moderately soluble, rendered it quite pure, and the substance then melted sharply at  $148^{\circ}$ :

0.1624 gave 0.4257  $\text{CO}_2$  and 0.0818  $\text{H}_2\text{O}$ .  $\text{C}=71.5$ ;  $\text{H}=5.61$ .

0.1884 „ 12.2 c.c.  $\text{N}_2$  at  $26^{\circ}$  and 742 mm.  $\text{N}=7.3$ .

$\text{C}_{12}\text{H}_{11}\text{O}_3\text{N}$  requires  $\text{C}=71.64$ ;  $\text{H}=5.47$ ;  $\text{N}=7.00$  per cent.

The *N-nitroso*-derivative, prepared in the usual manner, crystallised from alcohol in almost colourless needles melting at  $175^{\circ}$ :

0.1448 gave 15.15 c.c.  $\text{N}_2$  at  $22^{\circ}$  and 757 mm.  $\text{N}=12.1$ .

$\text{C}_{12}\text{H}_{10}\text{O}_3\text{N}_2$  requires  $\text{N}=12.17$  per cent.

The *benzoyl* derivative,  $\text{C}_{19}\text{H}_{15}\text{O}_3\text{N}$ , forms colourless plates, sparingly soluble in alcohol and melting at  $252^{\circ}$ .

9-Methyl- $\psi$ -1:8-isonaphthoxazone was prepared from 6-nitro-7-methylcoumarin, the same precautions being taken as in the case of the preparation of the unsubstituted naphthoxazone. The product amounted to 3 grams from 8 grams of the nitro-derivative, the yield being approximately 35 per cent. of the theoretical. It crystallises in colourless needles melting at  $200^{\circ}$ :

0.1040 gave 6.4 c.c.  $\text{N}_2$  at  $30^{\circ}$  and 744 mm.  $\text{N}=6.8$ .

$\text{C}_{13}\text{H}_9\text{O}_2\text{N}$  requires  $\text{N}=6.63$  per cent.

The *picrate* crystallises in prismatic needles melting at  $209^{\circ}$ .

The *dichromate* crystallises from water in orange-yellow, flat prisms.

The *ferrocyanide* forms a chocolate-red, crystalline powder.

The *platinichloride* crystallises in deep yellow, small needles.

The *aurichloride* forms an amorphous, yellow precipitate.

The *mercurichloride* crystallises in soft, colourless, woolly needles.

The *potassium mercuri-iodide* forms clusters of pale yellow, prismatic needles.

5:6:7:8-Tetrahydro-9-methyl- $\psi$ -1:8-isonaphthoxazone, prepared from the corresponding methylnaphthoxazone by reduction with tin and hydrochloric acid, crystallises in golden-yellow needles melting at  $180^{\circ}$ :

0.1650 gave 9.9 c.c.  $\text{N}_2$  at  $27^{\circ}$  and 751 mm.  $\text{N}=6.75$ .

$\text{C}_{13}\text{H}_{13}\text{O}_2\text{N}$  requires  $\text{N}=6.51$  per cent.

The *nitroso*-derivative,  $\text{C}_{13}\text{H}_{12}\text{O}_3\text{N}_2$ , forms a colourless, crystalline powder melting at  $155^{\circ}$ .

4:9-Dimethyl- $\psi$ -1:8-isonaphthoxazone was obtained in a 20 per cent. yield by heating 6-nitro-4:7-dimethylcoumarin (m. p.  $250^{\circ}$ ) with glycerol and sulphuric acid under the usual conditions. It crystallises from warm alcohol in silky needles melting at  $238^{\circ}$ :

0.1249 gave 7 c.c.  $N_2$  at  $27^\circ$  and 748 mm.  $N=6.3$ .

$C_{14}H_{11}O_2N$  requires  $N=6.20$  per cent.

The *picrate* crystallises in yellow needles melting at  $197^\circ$ .

The *dichromate* forms a dark red, crystalline powder.

The *ferrocyanide* forms intense red, small prisms decomposing above  $300^\circ$ .

The *methiodide*,  $C_{15}H_{14}O_2NI$ , crystallises from water in dark brown needles melting at  $195^\circ$ .

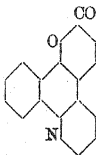
5 : 6 : 7 : 8-Tetrahydro-4 : 9-dimethyl- $\psi$ -1 : 8-isonaphthoxazone crystallises from alcohol in bright yellow needles melting at  $190^\circ$ . It is practically insoluble in hot water:

0.1438 gave 7.8 c.c.  $N_2$  at  $26^\circ$  and 748 mm.  $N=6.15$ .

$C_{14}H_{15}O_2N$  requires  $N=6.10$  per cent.

The *nitroso*-derivative,  $C_{14}H_{14}O_3N_2$ , prepared by adding a very dilute solution of sodium nitrite to a solution of the base in dilute hydrochloric acid at  $0^\circ$ , forms a colourless powder melting at  $161^\circ$ .

$\psi$ -Benzo-1:8-isonaphthoxazone,



The starting point in the synthesis of this substance is 6-nitro-1:2- $\alpha$ -naphthapyrone,  $C_{13}H_7O_4N$ , which does not appear to have been described before. It was prepared by the ordinary process of nitrating 1:2- $\alpha$ -naphthapyrone dissolved in glacial acetic acid, adding concentrated sulphuric acid, and warming the mixture on the water-bath. It separates from hot glacial acetic acid in pale yellow nodules melting at  $197^\circ$ .

The assumption that the nitro-group enters position 6 is based on the fact that the 6-nitro-derivative is formed first in the nitration of 4-methyl-1:2- $\alpha$ -naphthapyrone (Dey, T., 1915, 107, 1613).

$\psi$ -Benzo-1:8-isonaphthoxazone crystallises in soft, pale yellow needles melting at  $243^\circ$ . The yield amounted to 30 per cent. of the weight of the nitro-compound employed:

0.1490 gave 7.8 c.c.  $N_2$  at  $24.5^\circ$  and 759 mm.  $N=5.9$ .

$C_{16}H_9O_2N$  requires  $N=5.65$  per cent.

4-Methyl- $\psi$ -benzo-1:8-isonaphthoxazone was prepared from 6-nitro-4-methyl-1:2- $\alpha$ -naphthapyrone, and it exhibited the same

characteristics as the foregoing compound. The yield in one instance amounted to 50 per cent. of the theoretical.

It crystallises in pale yellow needles melting at  $234^{\circ}$ :

0.2291 gave 11.4 c.c.  $N_2$  at  $24^{\circ}$  and 759 mm.  $N=5.6$ .

$C_{17}H_{11}O_2N$  requires  $N=5.36$  per cent.

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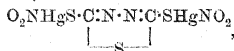
[Received, March 15th, 1919.]

# *XL.—Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. Part V. Chain Compounds of Sulphur (continued).*

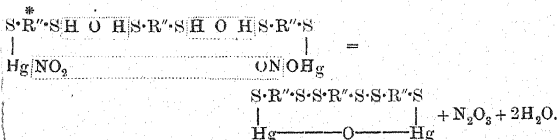
By SIR PRAFULLA CHANDRA RÂY and PRAFULLA CHANDRA GUHA.

THE present series of investigations has hitherto been confined to derivatives of monomercaptans; it has now been extended to those of the dimercaptans, of which 2:5-dithiol-1:3:4-thiodiazole may be taken as a typical representative.

When this dimercaptan is treated with mercuric nitrite, a dimercaptide dinitrite,



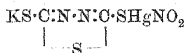
is not obtained, but the nitrous acid simultaneously disengaged oxidises the hydrogen atoms of two, three, four, and even six molecules of the dimercaptan, and the sulphur atoms become linked together and give rise to an interesting series of closed chain compounds. The maximum number of sulphur atoms forming the connecting link between two adjacent nuclei in the condensed complex molecule thus formed has so far been found to be twelve. Thus, in the case of a trinuclear condensation, we have



$R''$  denotes the bivalent group  $\begin{array}{c} \cdot C \cdot N \cdot N \cdot C \cdot \\ | \quad \quad | \\ \text{---S---} \end{array}$

The heavy molecule of the dimercaptide dinitrite cannot retain the load of two  $\text{NO}_2$  groups, and hence rupture takes place, as indicated by the dotted line, and a closed chain sulphoxy-derivative is finally formed with the liberation of nitrous fumes. The compounds thus generated are not, as a rule, nitrites. Some preparations, however, responded slightly to the nitrite tests, but the percentage of nitrogen due to the presence of nitrite was very low, proving that the proportion of the latter was insignificant. The occasional presence of some nitrite goes to establish the fact that the oxy-compound is in reality a decomposition product of the former.

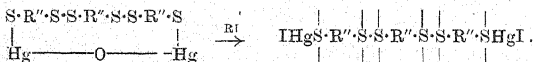
If, instead of the dimercaptan itself, its potassium salt is used, the tendency towards oxidation by nitrous acid is excluded and a mercaptide nitrite of the formula



is obtained.

The sulphoxy-compounds may be represented by the general formula  $(\text{C}_2\text{N}_2\text{S}_3)_x \cdot \text{Hg}_2\text{O}$ , where  $x=2, 3, 4$ , or 6. A condensation product of five molecules has not yet been obtained. It is not easy to explain why in one operation the value of  $x$  should be two and in others it should rise to six; possibly the concentration of the parent substances is the main determining factor. It has often been found that two preparations under similar conditions had identical compositions. In the majority of cases, the value of  $x$  was found to be three, occasionally two and four, and only rarely six.

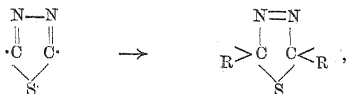
The preparations could not have been admixtures, because each of them strictly conformed to a definite formula. The most convincing proof of these compounds being of definite composition, however, is afforded by their reaction with the alkyl iodides. These sulphoxy-compounds behave exactly like mercaptide nitrites, and yield, as a rule, the corresponding sulphonium derivatives and, in a few cases, those with a less number of nuclei. The reducing action of the alkyl iodide removes the oxygen atom of the sulphoxy-ring, and, the bonds being thus snapped, an open-chain compound is formed, thus:



The six sulphur atoms of the chain now become quadrivalent by taking up the components of the alkyl iodide.

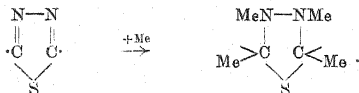
In this manner, a series of tetra-, hexa-, octa-, and dodeca-sulphonium compounds have been prepared. Each of these, with the exception of the propyl and butyl derivatives, is characterised by its crystalline character, and, moreover, its successive crops have the same melting point; the possibility of their being mixtures is thus precluded.

Another interesting point is the shifting of the double bonds, thus:



where R=methyl, ethyl, propyl, or butyl. As a rule, this is confined only to one nucleus. There is here evidently an extension of Thiele's theory to nitrogen compounds.

In one isolated instance, and that in the case of the reaction with methyl iodide, instead of there being a shifting of the double bonds, both the pairs of nitrogen and carbon atoms throughout the molecule were saturated by taking up additional methyl groups, thus:



## EXPERIMENTAL.

### *Sulphony-compounds.*

*General Method of Preparation.*—2:5-Dithiol-1:3:4-thiodiazole, prepared according to Busch's method (*Ber.*, 1894, **27**, 2518), in dilute alcoholic solution, was added drop by drop with vigorous stirring to a solution of mercuric nitrite, care being taken that the latter was always in excess. In this manner, a semi-gelatinous, pale yellow precipitate was obtained, which was washed with water and dried in a vacuum desiccator. The powdered, granular mass was then heated under reflux successively with alcohol and benzene to remove any adhering accidental organic impurities, namely, the parent dimercaptan or its oxidation product, the disulphide. This precaution was, however, found to be unnecessary. The compounds obtained in this way are always associated with some molecules of water.

*Potassium Salt of 2:5-Dithiol-1:3:4-thiodiazole and Mercuric Nitrite.*

With an aqueous solution of the potassium salt, a compound of the formula  $\text{KS}\cdot\text{C}\cdot\text{N}\cdot\text{N}\cdot\text{C}\cdot\text{SHgNO}_2$   $\left[ \begin{array}{c} \text{---S---} \end{array} \right]$

with  $12\text{H}_2\text{O}$  is obtained. Analysis of the substance gave:

Found:  $\text{Hg}=31.50$ ;  $\text{S}=13.89$ ;  $\text{C}=3.53$ ;  $\text{H}=5.34$ .\*

$\text{C}_2\text{O}_2\text{N}_3\text{S}_3\text{HgK}\cdot 12\text{H}_2\text{O}$  requires  $\text{Hg}=30.81$ ;  $\text{S}=14.79$ ;  $\text{C}=3.70$ ;  $\text{H}=3.70$  per cent.

*2:5-Dithiol-1:3:4-thiodiazole and Mercuric Nitrite: Formation of*

*the Dinuclear Sulphoxy-compound,*  $\text{S}\cdot\text{C}_2\text{N}_2\text{S}\cdot\text{S}_2\cdot\text{C}_2\text{N}_2\text{S}\cdot\text{S}$   
 $\left| \begin{array}{c} \text{Hg} \text{---} \text{O} \text{---} \text{Hg} \end{array} \right| \cdot 3\text{H}_2\text{O}.$

Found:  $\text{Hg}=52.57$ ,  $52.42$ ;  $\text{S}=23.76$ ;  $\text{N}=7.36$ .

$\text{C}_4\text{ON}_4\text{S}_6\text{Hg}_2\cdot 3\text{H}_2\text{O}$  requires  $\text{Hg}=52.22$ ;  $\text{S}=25.07$ ;  $\text{N}=7.31$  per cent.

*Trinuclear Sulphoxy-compound,*  $\text{S}\cdot\text{C}_2\text{N}_2\text{S}\cdot\text{S}\cdot\text{C}_2\text{N}_2\text{S}\cdot\text{S}_2\cdot\text{C}_2\text{N}_2\text{S}\cdot\text{S}$   
 $\left| \begin{array}{c} \text{Hg} \text{---} \text{O} \text{---} \text{Hg} \end{array} \right| \cdot \text{Hg}$

In this case, each distinct preparation gave the compound associated with 8, 5, and 2 molecules of water respectively.

*Compound with  $8\text{H}_2\text{O}$ .*

Found:  $\text{Hg}=40.21$ ;  $\text{S}=27.56$ ;  $\text{C}=8.50$ ;  $\text{N}=8.18$ .

$\text{C}_6\text{ON}_6\text{S}_9\text{Hg}_3\cdot 8\text{H}_2\text{O}$  requires  $\text{Hg}=39.85$ ;  $\text{S}=28.69$ ;  $\text{C}=7.17$ ;  $\text{N}=8.37$  per cent.

*Compound with  $5\text{H}_2\text{O}$ .*

Found:  $\text{Hg}=42.07$ ;  $\text{S}=30.21$ ;  $\text{N}=9.36$ .

$\text{C}_6\text{ON}_6\text{S}_9\text{Hg}_3\cdot 5\text{H}_2\text{O}$  requires  $\text{Hg}=42.11$ ;  $\text{S}=30.31$ ;  $\text{N}=8.84$  per cent.

*Compound with  $2\text{H}_2\text{O}$ .*

Found:  $\text{Hg}=45.33$ ;  $\text{S}=31.40$ ;  $\text{N}=9.52$ .

$\text{C}_6\text{ON}_6\text{S}_9\text{Hg}_3\cdot 2\text{H}_2\text{O}$  requires  $\text{Hg}=44.65$ ;  $\text{S}=32.14$ ;  $\text{N}=9.38$  per cent.

On repeating the preparation, the same trinuclear condensation

\* The percentage of hydrogen is often too high as traces of mercury vapour are apt to be carried over to the calcium chloride tube; in many cases, therefore, the value of hydrogen has not been given.



product was obtained, although sometimes in an impure form. Thus in one preparation there was found  $\text{Hg}=42.52$ ,  $\text{S}=34.54$ , and in another,  $\text{Hg}=43.72$ ,  $\text{S}=31.53$ . However, on treating each of these with the alkyl iodides, the same sulphonium compound was obtained (see p. 546).

*Tetranuclear Sulphoxy-compound,  $(\text{C}_2\text{N}_2\text{S}_3)_4, \text{Hg}_2\text{O}$ .*

*Compound with  $3\text{H}_2\text{O}$ .*

Found:  $\text{Hg}=37.94$ ;  $\text{S}=37.54$ ;  $\text{N}=11.48$ .

$\text{C}_8\text{ON}_8\text{S}_{12}\text{Hg}_2, 3\text{H}_2\text{O}$  requires  $\text{Hg}=37.67$ ;  $\text{S}=36.16$ ;  $\text{N}=10.55$  per cent.

*Compound with  $5\text{H}_2\text{O}$ .*

Found:  $\text{Hg}=37.21$ ;  $\text{S}=35.13$ ;  $\text{N}=9.55$ .

$\text{C}_8\text{ON}_8\text{S}_{12}\text{Hg}_2, 5\text{H}_2\text{O}$  requires  $\text{Hg}=36.43$ ;  $\text{S}=34.97$ ;  $\text{N}=10.2$  per cent.

*Hexanuclear Sulphoxy-compound,  $(\text{C}_2\text{N}_2\text{S}_3)_6, \text{Hg}_2\text{O}, 7\text{H}_2\text{O}$ .*

Found:  $\text{Hg}=28.52$ ;  $\text{S}=39.82$ ;  $\text{N}=11.59$ .

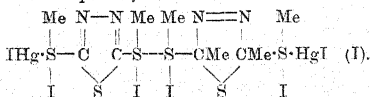
$\text{C}_{12}\text{ON}_{12}\text{S}_{18}\text{Hg}_2, 7\text{H}_2\text{O}$  requires  $\text{Hg}=27.97$ ;  $\text{S}=40.28$ ;  $\text{N}=11.75$  per cent.

*Reaction with the Alkyl Iodides.*

*General Method of Preparation.*—The above sulphonyl-derivatives were heated with the alkyl iodides on a water-bath under reflux for several hours, the product being allowed to remain overnight. Sometimes a crystalline mass, and occasionally a heavy, dark brown oil, settled at the bottom; the excess of alkyl iodide was decanted or distilled off, and the product dissolved in the minimum quantity of acetone and the solution filtered from the insoluble matter whenever necessary. On adding ether to the filtrate, a pale yellow, mealy, crystalline precipitate was obtained, and this process was repeated in order further to purify the substance.

*Dinuclear Condensation.*

*The Compound,  $\text{C}_4\text{ON}_4\text{S}_6\text{Hg}_2$ , and Methyl Iodide: Formation of the Compound,*



The product melted at  $101-102^\circ$ .

Found: Hg=25.94; I=49.23; C=7.75.

$C_{10}H_{18}N_4S_6Hg_2I_6$  requires Hg=25.84; I=49.33; C=7.75 per cent.

The corresponding compound with ethyl iodide (II) was sparingly soluble in acetone, and was therefore purified by crystallisation from the boiling solvent; it melted at  $107^\circ$ .

Found: Hg=24.19, 24.58; I=43.20\*; C=11.25, 11.42; N=3.53.  
 $C_{16}H_{30}N_4S_6Hg_2I_6$  requires Hg=24.51; I=46.69; C=11.76; N=3.43  
 per cent.

The corresponding dinuclear tetrasulphonium compounds with *n*-propyl and *n*-butyl iodides did not crystallise, but consisted of dark brown, pasty masses, which were purified by repeated precipitation with ether from acetone solution.

*Compound with n-propyl iodide (III).*

Found: Hg=23.89; I=44.74; C=14.05.

$C_{22}H_{42}N_4S_6Hg_2I_6$  requires Hg=23.31; I=44.40; C=15.38 per cent.

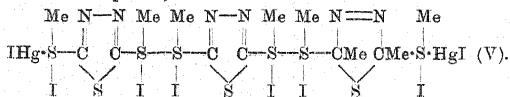
*Compound with n-butyl iodide (IV).*

Found: Hg=21.77; I=41.75; C=17.66; N=3.11.

$C_{28}H_{54}N_4S_6Hg_2I_6$  requires Hg=22.22; I=42.33; C=18.60; N=3.11  
 per cent.

### *Trinuclear Condensation.*

*The Compound,  $C_6ON_6S_6Hg_3$ , and Methyl Iodide: Formation of the Compound,*



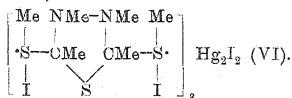
The product of the interaction was an oil. It was dissolved in hot acetone, and the solution, on cooling, deposited a crystalline mass, which when recrystallised from hot acetone yielded needle-shaped crystals melting at  $101$ — $102^\circ$ , identical with the compound,  $C_{10}H_{18}N_4S_6Hg_2I_6$ , described above. The original mother liquor, on concentration, gave two successive crops melting at  $85$ — $86^\circ$ .

Found: Hg=21.55; C=8.66.

$C_{14}H_{24}N_6S_6Hg_3I_8$  requires Hg=20.20; C=8.48 per cent.

\* As a large quantity of copper powder has to be used and the process is a tedious one, the values for iodine and sulphur are sometimes too low (see T., 1916, 109, 611).

*Compound with Methyl Iodide in which all the Double Bonds are Saturated,*



The method of preparation and purification was the same as in the case of the preceding compound. It is a white, crystalline substance melting at  $94^\circ$ .

Found: Hg=18.24; S=11.36; C=13.15; H=2.54.

$\text{C}_{24}\text{H}_{54}\text{N}_6\text{S}_9\text{Hg}_2\text{I}_8$  requires Hg=18.78; S=13.52; C=13.52; H=2.53 per cent.

The formation of this type of compound has been observed only in this one instance.

*Compound with n-Propyl Iodide (VII).*

This conforms to the ordinary type.

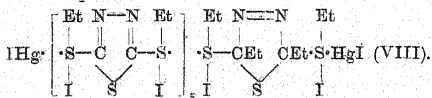
Found: Hg=18.54; I=44.61; C=16.47.

$\text{C}_{30}\text{H}_{56}\text{N}_6\text{S}_9\text{Hg}_2\text{I}_8$  requires Hg=18.14; I=46.1; C=16.33 per cent.

As will be noticed, the trinuclear sulphonyl-compound gives with methyl iodide compounds I and V, the latter being the chief product. This tendency towards the formation of the dinuclear tetra-sulphonium compound from the higher nuclear sulphonyl-compounds is particularly noticeable in the case of the reaction with ethyl iodide, when only the dinuclear sulphonium compound (II) is obtained, even from tri- and tetra-nuclear sulphonyl-derivatives. In all these cases of formation of a lower member from the higher sulphonyl-compounds, a dark brown, pasty substance with a penetrating odour and lachrymatory properties was always produced, which resisted all attempts at purification.

#### Hexanuclear Condensation.

*The Compound,  $\text{C}_{12}\text{ON}_{12}\text{S}_{18}\text{Hg}_2$ , and Ethyl Iodide: Formation of the Compound,*



This melted at  $90-91^\circ$ .

Found: I=50.03; N=3.90; C=13.14.

$C_{40}H_{70}N_{12}S_{18}Hg_2I_{14}$  requires I=51.20; N=4.84; C=13.82 per cent.

It will thus be seen that the type persists throughout, in that the alteration in the position of the double bond is limited to only one nucleus of the chain.

In the previous communications, the compounds there described were tentatively classed under the sulphonium group, although no direct proof could be adduced in support of this view. One of the purest compounds of this series, namely,  $MeEtS_2.HgI_2.EtI$  (T., 1916, 109, 606), was selected for molecular weight determination in acetone solution by the ebullioscopic method; the value obtained was 712, that required by theory being 718. It is thus evident that the constitution is atomic (compare Hilditch and Smiles, T., 1907, 91, 1396).

A study of the physical properties of the interesting polysulphonium compounds treated of in this paper is being undertaken which, it is hoped, will throw additional light on their constitution.

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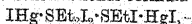
## XII.—*Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. Part VI. Chain Compounds of Sulphur (continued).*

By SIR PRAFULLA CHANDRA RAY.

THE present investigation deals with the chain compounds of sexavalent sulphur. On treating the product of the interaction of thiocarbamide and mercuric nitrite, namely, the sulfoxynitrite,

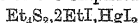
$NH_2.C(NH).S(HgNO_2) < \begin{smallmatrix} Hg \\ O \end{smallmatrix}$  (T., 1917, 111, 102), with ethyl

iodide, a yellow, crystalline substance was obtained which was soluble in acetone, and, on purification by precipitation with ether, melted at 98—100°. Analysis proved it to conform to the formula  $Et_2S_2.EtI_2.HgI_2$ ; in other words, it is a member of the disulphonium series already described (T., 1916, 109, 134) with an additional molecule of mercuric iodide in combination, to which should be assigned the constitutional formula



one of the sulphur atoms in the chain becoming sexavalent. The formation of this compound suggested the possibility of the direct conversion of all the members of the series  $RR'S_2R'I, HgI_2$  into  $RR'S_2R'I, 2HgI_2$ . This anticipation has been realised with one notable exception. When the alkyl group happens to be methyl, combination with an extra molecule of mercuric iodide does not take place. The presence of the radicle ethyl, on the other hand, favours the combination. Thus in the above series, where  $R=Me$  and  $R'=Pr^a$  or butyl, the extra valencies of the sulphur atom are not revived, but if  $R'$  happens to be ethyl, this anomaly disappears. To what extent the ethyl group favours the increase in valency will be evident from a typical case. When mercury ethyl-mercaptide nitrite,  $EtS \cdot HgNO_2$ , is treated with methyl iodide, by an interchange of the radicle, the compound,  $EtMeS_2, HgI_2, MeI$ , is obtained (T., 1916, 109, 603); but in this case, although there are two methyl groups, the presence of a single ethyl group is sufficient to counteract the prejudicial influence of the former, and the compound,  $EtMeS_2, MeI, 2HgI_2$ , is readily formed.

The marked genetic affinity of the radicle ethyl for sulphur and its influence on the increase in its valency is further evidenced by the fact that a compound of the empirical formula



has also been obtained from ethyl sulphide by its reaction with ethyl iodide and mercuric iodide. On repeating Smiles's experiment (T., 1900, 77, 161), under slightly altered conditions, with a view to ascertain the maximum valency of sulphur, it was noticed that whilst the main product was the compound,  $Et_3SI, HgI_2$ , as found by this author, there was always a considerable amount of a shining, crystalline substance, practically insoluble in cold acetone. As it had a sharp melting point when crystallised from hot acetone, it was analysed, with the result that the formula given above was established. What evidently happens is that under the joint action of mercuric iodide and ethyl iodide, or rather their ions, the bivalent sulphur atoms of two adjacent molecules of ethyl sulphide become sexavalent, with the formation of the compound,  $SEt_3I_2 \cdot SEt_3I \cdot HgI$ .

It is remarkable that if, in the above reaction, ethyl iodide is substituted by methyl, propyl, or butyl iodide, the product in each case is completely soluble in acetone and conforms to the general formula  $Et_3RSI, HgI_2$ , but no product of the fusion of two ethyl sulphide molecules is formed. The differential property of ethyl as compared with other alkyl radicles is thus brought into relief.

It was expected that the general method of the preparation of

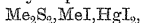
the disulphonium compounds already described, namely, the treatment of ethyl mercurimercaptide nitrite,  $\text{EtS}\cdot\text{HgNO}_2$ , with ethyl iodide, should also yield the chain compound containing both the sulphur atoms in the sexavalent state. This expectation has also been realised. The latter compound is produced in such small amount that on previous occasions its formation was overlooked. It has already been shown that ethyl disulphide, ethyl iodide, and mercuric iodide also combine directly to yield the disulphonium compound,  $\text{Et}_2\text{S}_2\cdot\text{HgI}_2\cdot\text{EtI}$  (*loc. cit.*). Recently, this preparation has been repeated, and it has been found that the sexavalent disulphur compound is also formed in considerable quantity along with the former. It is thus evident that both the chain compounds, containing quadri- and sexa-valent sulphur respectively, are formed simultaneously.

It is of interest to note that Smiles and Hilditch, who treated an acetone solution of molecular proportions of ethyl disulphide and mercuric iodide with ethyl iodide, obtained diethylthioethylsulphonium dimercuric iodide,  $(\text{C}_2\text{H}_5)_3\text{S}_2\text{I}_2\cdot 2\text{HgI}_2$  (T., 1907, 91, 1396). It is evidently the same compound as has been described above.

An explanation may be offered as to why it is that in the first series of compounds only one of the two atoms of sulphur exists in the sexavalent condition; here the quadrivalent sulphur, being already weighted with the heavy load of the ions  $\text{HgI}'$  and  $\text{I}'$ , has lost the capacity of taking up an additional charge; in other words, of acquiring the maximum valency. In the solitary instance, however, in which both the sulphur atoms happen to be sexavalent, it will be noticed that there is only one set of  $\text{HgI}'$  and  $\text{I}'$  ions; the sulphur atom combined with the latter has attached to it three additional comparatively light ethyl radicles, whereas the other sulphur atom, not having to bear the load of the heavy  $\text{HgI}$ -group, is in a position to take up three ethyl groups and two iodine atoms. Facts are already known which go to support the view that the maximum valency of an element is often conditional on the load of the radicles. The author hopes in a succeeding communication to show that platinum when attached to the radicle of 5-thiol-2-thio-3-phenyl-2:3-dihydro-1:3:4-thiodiazole, is in the tervalent condition. It is none the less inexplicable why the light radicle methyl should stand in the way of one of the atoms of sulphur attaining its maximum valency. The anomalous behaviour of the first member of the alkyl series is, however, well known.

## EXPERIMENTAL.

The general method of preparation of the series  $R_2S_2, RI, 2HgI_2$  has already been incidentally described. These members are readily obtained by dissolving the corresponding disulphonium compound in acetone and adding mercuric iodide to the solution until no more is absorbed. The golden-yellow liquid is decanted from the undissolved iodide, and, on adding ether, a copious deposit of yellow, mealy crystals is obtained. Solution in acetone and precipitation by ether is repeated until the product gives a fairly sharp melting point. It has been found that in some instances, especially in the case of the methylsulphonium compound,



the acetone solution at first takes up a considerable quantity of mercuric iodide, but purification by the above process gradually removes all the mechanically held salt.

*Compound*  $Et_2S_2, EtI, 2HgI_2$ .—(a) From the sulphoxynitrite derivative of thiocarbamide and ethyl iodide. The substance melted at  $98^\circ$ :

0.3656 gave 0.1250 Hg, 0.3540 AgI, and 0.1029  $BaSO_4$ .  
Hg=34.19; I=52.32; S=3.87.

0.2442 gave 0.0570  $CO_2$  and 0.0356  $H_2O$ . C=6.37; H=1.62.

(b) By the direct union of mercuric iodide with the compound  $Et_2S_2, EtI, HgI_2$ . The substance melted at  $100-101^\circ$ :

0.2118 gave 0.0711 Hg. Hg=33.57.

0.2118 „ 0.0532  $CO_2$  and 0.0325  $H_2O$ . C=6.85; H=1.71.

$C_6H_{15}I_5S_2Hg_2$  requires Hg=33.73; I=53.54; S=5.4; C=6.07;  
H=1.26 per cent.

*Compound*  $MeEtS_2, EtI, 2HgI_2$  (m. p.  $38-40^\circ$ ):

0.3840 gave 0.1236 Hg and 0.3768 AgI. Hg=32.19; I=53.03.

0.2094 „ 0.0452  $CO_2$  and 0.0466  $H_2O$ . C=5.87; H=2.47.

$C_6H_{13}I_5S_2Hg_2$  requires Hg=34.14; I=54.19; C=5.12; H=1.11  
per cent.

*Compound*  $MeEtS_2, MeI, 2HgI_2$  (m. p.  $50-55^\circ$ ):

0.2467 gave 0.2483 AgI and 0.0840 Hg. Hg=34.05; I=54.39.

0.1428 „ 0.0286  $CO_2$  and 0.0211  $H_2O$ . C=5.46; H=1.64.

$C_4H_{11}I_5S_2Hg_2$  requires Hg=34.55; I=54.84; C=4.14; H=0.95  
per cent.

*Compound*  $EtPr^sS_2, Pr^sI, 2HgI_2 + C_3H_6O$  (m. p.  $30-31^\circ$ ).—This compound contains one molecular proportion of acetone:

0.4410 gave 0.1400 Hg. Hg=31.75.

0.1629 „ 0.0586 CO<sub>2</sub> and 0.0352 H<sub>2</sub>O. C=9.81; H=2.40.

C<sub>8</sub>H<sub>19</sub>I<sub>5</sub>S<sub>2</sub>Hg<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>O requires Hg=31.45; C=10.38; H=1.97  
per cent.

*Compound* Et(C<sub>4</sub>H<sub>9</sub>)S<sub>2</sub>.C<sub>4</sub>H<sub>9</sub>I.2HgI<sub>2</sub>+1.5C<sub>3</sub>H<sub>6</sub>O.—The substance had the consistency of treacle, and contained 1.5 molecular proportions of acetone:

0.3879 gave 0.1153 Hg and 0.3272 AgI. Hg=29.72; I=45.58.

0.1340 „ 0.0649 CO<sub>2</sub> and 0.0363 H<sub>2</sub>O. C=13.21; H=3.01.

C<sub>10</sub>H<sub>23</sub>I<sub>5</sub>S<sub>2</sub>Hg<sub>2</sub>, 1.5C<sub>3</sub>H<sub>6</sub>O requires Hg=30.10; I=47.79; C=13.10;  
H=2.41 per cent.

*Compound* containing two sexavalent sulphur atoms (m. p. 146—147°). It was very sparingly soluble in cold acetone, but fairly readily so in the boiling solvent:

0.2991 gave 0.063 Hg and 0.2916 AgI. Hg=21.06; I=52.69.

0.4032 „ 0.8400 Hg and 0.2042 BaSO<sub>4</sub>. Hg=20.86; S=6.96.

0.1930 „ 0.1068 CO<sub>2</sub> and 0.0538 H<sub>2</sub>O. C=15.09; H=3.09.

C<sub>12</sub>H<sub>30</sub>I<sub>4</sub>S<sub>2</sub>Hg requires Hg=21.14; I=53.70; S=6.77; C=15.22;  
H=3.17 per cent.

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## XLII.—Mercuric Sulphoxychloride.

By SIR PRAFULLA CHANDRA RÂY and PRAFULLA KUMAR SEN.

THE close analogy between mercuric chloride and nitrite has been found to hold good throughout the investigations carried on from 1898 onwards. Thus, whilst mercuric nitrate with sodium sulphate at once gives an abundant yellow precipitate of the oxysulphate, the chloride and the nitrite fail to give it (T., 1897, 71, 1103). The explanation lies in the fact that the latter salts are very feebly ionised in solution, and thus have no tendency to yield basic compounds. Ammonia, amines, and even a class of alkaloids have been found to behave towards mercuric nitrite in a manner similar to their action on the chloride (T., 1913, 103, 3; 1917, 111, 507).

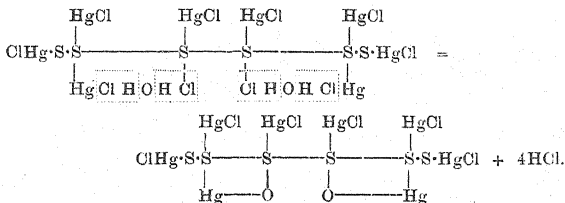
The substituted thiocarbamides, thiocarbimides, thiobenzamide, etc., have been shown to give rise to a purely inorganic sulphony-nitrite of the empirical formula [3(SHgNO<sub>2</sub>),HgO]<sub>2</sub>, which is in



reality a chain compound containing six atoms of sulphur linked together (T., 1917, 111, 104).

An attempt has been made to isolate the radicle  $(\text{SHgCl})_2$ , which would be the analogue of mercuric iodosulphide,  $(\text{SHgI})_2$  (*loc. cit.*, p. 109), by treating mercuric chloride with some typical thio-compounds named above, as also thioacetic acid and ammonium dithiocarbamate. It was expected that in each case the radicle,  $\text{SHgCl}$ , would become detached from the parent substance and lead an independent existence. This expectation has been realised, but in a qualified sense. The radicle,  $\text{SHgCl}$ , no sooner separates out than it assumes the form  $[3(\text{SHgCl}), \text{HgO}]_2$ , which is the exact analogue of the oxynitrite. It has been shown already that the complex nitrite containing several nitro-groups, by the elimination of nitrogen trioxide, readily yields the oxynitrite.

It is not easy at first to understand how the chloride would also give rise to an oxy-salt. The explanation is obvious when it is considered that water takes part in the reaction; the compound  $[3(\text{SHgCl}), \text{HgO}]_2$  is formed thus:

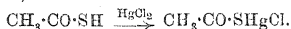


In other words, as soon as the radicle,  $\text{SHgCl}$ , is formed, three groups take up an additional molecule of mercuric chloride, that is, the radicles  $\text{HgCl}$  and  $\text{Cl}$  and a molecule of water simultaneously take part in the reaction, four molecules of hydrogen chloride are generated, and the oxygen atom forms the connecting link between the mercury atom, the neighbouring sulphur atom, and the two symmetrical complexes coalescing into a single molecule.

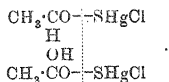
It is necessary to point out that whilst the radicle,  $\text{SHgNO}_2$ , has often a tendency to part company with the parent substance, the radicle,  $\text{SHgCl}$ , on the other hand, often remains attached to it. Thus thiocarbamide when acted on by mercuric chloride yields the compound  $\text{NH}_2 \cdot \text{C} \cdot \text{NH} \cdot \text{SHgCl}, \text{HCl}$ , which is actually a hydrochloride, as will be shown in a subsequent communication. If, however, thiocarbamide is converted into its diacetyl derivative and then treated with mercuric chloride, the molecule is ruptured,

with the detachment of the radicle,  $\text{SHgCl}$ , and the formation of the oxychloride. *s*-Diphenylthiocarbamide also behaves similarly. Evidently the introduction of the negative radicles, acetyl and phenyl, neutralises the basic character of the compound due to the presence of an amino- and imino-group, and deprives it of the power of forming a hydrochloride, in which character alone it is stable.

It is a characteristic diagnostic property of mercaptans, real and potential, that with mercuric nitrite and chloride they yield the mercaptide nitrite and chloro-mercaptide respectively. Thioacetic acid, although an acid, contains the group  $\text{SH}$  and behaves like a typical mercaptan, thus:



As soon as this compound is formed, it acts on a molecule of water, and the scission takes place as shown by the dotted line, a



molecule of acetaldehyde and acetic acid being formed.

Ammonium dithiocarbamate assumes the tautomeric form,  $\text{SH}\cdot\text{C}(\text{:NH})\cdot\text{SNH}_2$ , and both the radicles  $\text{SH}$  and  $\text{SNH}_2$  with mercuric chloride yield  $\text{SHgCl}$ , which separates out.

Allylthiocarbimide,  $\text{C}_3\text{H}_5\cdot\text{NCS}$ , combines with the elements of mercuric chloride, and the compound,  $\text{C}_3\text{H}_5\cdot\text{N}\cdot\text{C}\cdot\text{SCl}\cdot\text{HgCl}$ , is temporarily formed, the sulphur atom becoming quadrivalent. As this configuration is unstable, a rupture takes place along the line of least resistance, the radicle,  $\text{:SCl}\cdot\text{HgCl}$ , decomposes into the stable radicle,  $\text{SHgCl}$ , and chlorine, whilst the organic portion of the complex,  $\text{R}\cdot\text{N}\cdot\text{C}\cdot$ , with a molecule of water yields a primary amine and carbon monoxide.

#### EXPERIMENTAL.

*Method of Preparation.*—The thio-compound in aqueous or alcoholic solution, as the case might be, was added in a thin stream by means of a pipette to an aqueous solution of mercuric chloride with vigorous stirring, care being taken that the latter ingredient was always in large excess.

A granular, white precipitate was obtained, which was washed first with water and then with alcohol, and finally dried in a vacuum over sulphuric acid. A special precaution is necessary in the case of allylthiocarbimide. If an alcoholic solution of it is

added to an aqueous solution of mercuric chloride, the white precipitate is obtained, but, at the same time, heavy, oily globules begin to settle down at the bottom, and it is not always easy to separate them from the sulphoxychloride. It is best to add the dilute alcoholic solution of the allylthiocarbimide to an alcoholic solution of mercuric chloride. The mixture remains clear, but on copious dilution with water and stirring, the white precipitate begins to appear. The mixture is allowed to remain overnight, and the product collected and treated as before.

The interaction of each of the above-mentioned thio-compounds and mercuric chloride was repeated several times, and the composition throughout was found to be identical. It is therefore not necessary to give the analysis of each preparation; that of one or two typical ones are given below.

*Action of Mercuric Chloride on Diacetylthiocarbamide.*

Diacetylthiocarbamide (Kohmann, *J. Amer. Chem. Soc.*, 1915, **37**, 2130) was dissolved in water and added drop by drop to a solution of mercuric chloride from a pipette with constant stirring. A white, amorphous precipitate was formed which, on remaining for twenty-four hours, became granular. It was collected, washed with water, and dried:

0.3276 gave 0.2591 Hg and 0.1354 AgCl. Hg=79.1; Cl=10.2.

0.2419 „ 0.1048 AgCl and 0.1647 BaSO<sub>4</sub>. Cl=10.7; S=9.4.  
[3(SHgCl),HgO]<sub>2</sub> requires Hg=78.7; Cl=10.5; S=9.4 per cent.

The absence of carbon and hydrogen was confirmed by repeated combustion.

*Action of Mercuric Chloride on s-Diphenylthiocarbamide.*

The hot alcoholic solution of *s*-diphenylthiocarbamide was added to a solution of mercuric chloride, and the mixture was heated on a boiling-water bath under reflux for several hours. The white precipitate was collected, washed with hot alcohol and finally with water, and dried:

0.2591 gave 0.1097 AgCl and 0.1698 BaSO<sub>4</sub>. Cl=10.47; S=9.0.

0.3684 „ 0.2902 Hg. Hg=78.8.

*Mercuric Chloride and Thioacetic Acid.*

*Result of analysis:*

0.2587 gave 0.2370 HgS. Hg=79.0.

0.1465 „ 0.0625 HgCl and 0.1070 BaSO<sub>4</sub>. Cl=10.55;  
S=10.0.

*Mercuric Chloride and Allylthiocarbimide.**Result of analysis:*0.3402 gave 0.2631 Hg.  $Hg=77.34$ .0.2795 „ 0.1285 AgCl and 0.1818 BaSO<sub>4</sub>.  $Cl=11.4$ ;  $S=8.9$ .

The absence of carbon was shown by combustion analysis.

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XLIII.—*The Preparation of Cadmium Suboxide.*

By HENRY GEORGE DENHAM.

VARIOUS suboxides of cadmium have long ago been described (Tanatar, *Zeitsch. anorg. Chem.*, 1901, **27**, 433; Morse and Jones, *Amer. Chem. J.*, 1890, **12**, 488, etc.), although other investigators have thrown doubt on the existence of these suboxides. The following experiments describe the efforts made to prepare a suboxide of cadmium in as pure a state as has been the case with lead suboxide.

*Decomposition of Cadmium Oxalate.*

The first method attempted was that described by Tanatar (*loc. cit.*), namely, the decomposition of the oxalate in a stream of carbon dioxide. A sample of cadmium oxalate ( $Cd=56.02$  per cent.) was heated at  $300^{\circ}$  in a rapid stream of carbon dioxide freed from traces of oxygen by passage through heated copper. At the end of forty-eight hours the evolution of gas ceased, and examination revealed a small quantity of a green material, unmistakably containing globules of cadmium, whilst the leading tubes were lined with a deposit of the volatilised metal. This experiment, many times repeated, always gave the same result.

Precisely similar results were obtained when the carbon dioxide was not employed, the evolved gases being removed by means of a Sprengel pump. Even when the total pressure of these gases did not exceed 1 mm., the same green, heterogeneous substance was produced. Analysis of this material always gave values closely approximating to  $Cd=96.5$  per cent. (Tanatar's  $Cd_4O$  contains  $Cd=96.56$  per cent.).

Tanatar and Levin (*loc. cit.*) also describe how the oxide,  $\text{Cd}_2\text{O}$ , was obtained by the decomposition of a basic oxalate under similar conditions. A repetition of their experiment always gave a heterogeneous grey mass containing free cadmium.

An attempt was then made to remove by distillation the excess of metal present in the decomposition product of the oxalate. The mixture was heated to  $350^\circ$  without undergoing any change in appearance. The pump was then put into requisition, and in ten hours a large deposit of cadmium had volatilised out of the oven, whilst the residue was a homogeneous green mass, in which the microscope was no longer able to detect free metal. The following analytical results were obtained:

Oxalate. Grams.	Green substance. Gram.	$\text{CdSO}_4$ . Gram.	Cd. per cent.
2.0	0.0362	0.0628	93.5
2.5	0.0592	0.1025	93.4
2.0	0.0809	0.1401	93.4

$\text{Cd}_2\text{O}$  requires  $\text{Cd}=93.36$  per cent.

The method therefore appears to give a green oxide, but owing to the strong reducing action of the evolved carbon monoxide and the difficulty of distilling out the free metal, the method is not satisfactory.

#### *Reduction by Hydrogen.*

An attempt was made to prepare the suboxide by reducing the brown oxide with hydrogen (see Glaser, *Zeitsch. anorg. Chem.*, 1903, 36, 1). At  $240^\circ$ , after twenty hours' reduction, the yellowish-green product appeared to be uniform, but the microscope clearly revealed globules of free metal. Reduction under varying conditions of temperature and pressure always led to this result. The excess of metal was afterwards removed by distillation, and a uniform, yellowish-green product obtained, in which the microscope revealed no sign of free metal. Analysis, however, showed that this substance was pure cadmium oxide ( $\text{CdO}$ ), the colour change being either superficial or due to a different molecular aggregation.

#### *Reduction by Carbon Monoxide.*

It has been shown by Brislee (T., 1908, 93, 162) that the time-reduction curve of cadmium oxide at  $300^\circ$ , with carbon monoxide as the reducing agent, shows a distinct break at a point which corresponds with the compound  $\text{Cd}_2\text{O}$ . Although it appeared

difficult to stop the reduction at the precise moment when the whole of the higher oxide had been reduced to the suboxide and none of the latter to the metal, it seemed feasible to carry through the reduction in such a way that the higher oxide was reduced to a mixture of the suboxide and metal, and this metal could then be removed by volatilisation.

An analysis of Brislee's time-reduction curve for  $300^{\circ}$  shows that the break occurs when the reduction has progressed for about twelve hours. An experiment was therefore carried out in which carbon monoxide was circulated for fourteen hours at  $300^{\circ}$  through two bulbs, each containing about 0.6 gram of cadmium oxide. One bulb was then sealed off, and the other heated in a vacuum for eighteen hours. The material in the first bulb was yellowish-green, containing visible globules of cadmium, whilst the second bulb gave a perfectly uniform, yellowish-green substance. Bulb I, contained  $\text{Cd}=90.4$  and bulb II  $\text{Cd}=87.5$ , whilst  $\text{CdO}$  requires  $\text{Cd}=87.57$  per cent. This experiment was repeatedly carried out at various temperatures between  $300^{\circ}$  and  $310^{\circ}$ , and in all cases the bulb sealed off before exhaustion contained a considerably higher percentage of cadmium than does  $\text{CdO}$ , approximating often to that of  $\text{Cd}_2\text{O}$ , but a moderately good pocket lens was sufficient in every case to show that the reduction product was heterogeneous and contained cadmium. Similarly, the bulb from which the excess of cadmium had been volatilised at the temperature of the experiment always gave a uniform, yellowish-green product exactly similar to that obtained when hydrogen was the reducing agent, and the composition of this was undoubtedly that of  $\text{CdO}$ . As a means of preparation of cadmium suboxide, this method therefore fails.

#### *Morse and Jones's Method.*

Morse and Jones (*loc. cit.*) have described how anhydrous cadmium chloride, when fused with cadmium, gives a product having the composition  $\text{Cd}_4\text{Cl}_7$ . This they consider to be possibly a mixture of  $3\text{CdCl}_2 + \text{CdCl}$ . On treatment with water, the product gave cadmous hydroxide, from which yellow cadmous oxide,  $\text{Cd}_2\text{O}$ , was readily obtained by dehydration. The author has repeated this work, and succeeded in reproducing the results described by Morse and Jones, but in spite of close attention to the details given in the original publication, he has never succeeded in converting more than 5 per cent. of the original chloride into suboxide, so that, as a practical method of preparing the suboxide in quantity, the method is not satisfactory.

In conclusion, it may be stated that the suboxide of cadmium may be obtained in small quantity by the method described by Morse and Jones, as well as by the decomposition of cadmium oxalate. The latter method, however, is only of use when the excess of metal, always formed during the decomposition, is distilled off in a vacuum, but the amount of residual cadmium suboxide is never more than 4 per cent. by weight of the original oxalate.

The author desires to place on record his appreciation of the facilities placed at his disposal by the Walter and Eliza Hall Trust for the prosecution of this research.

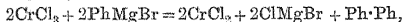
THE DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF QUEENSLAND,  
BRISBANE.

[Received, November 7th, 1918.]

#### XLIV.—*Formation of Diphenyl by the Action of Cupric Salts on Organometallic Compounds of Magnesium.*

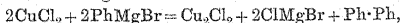
By JACOB KRIZEWSKY and EUSTACE EBENEZER TURNER.

A FEW years ago, it was shown (Bennett and Turner, T., 1914, 105, 1057) that chromic chloride reacted quantitatively with magnesium phenyl bromide in the sense of the equation



and the reaction was found to be a general one.

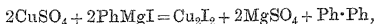
It has now been found that anhydrous cupric chloride behaves similarly to chromic chloride. Thus, when anhydrous cupric chloride is added to an ethereal solution of magnesium phenyl bromide, the following reaction occurs:



diphenyl being formed in almost the theoretical quantity. Furthermore, the preparation may be simplified, an equally good result being obtained by mixing, at the outset, magnesium turnings, ether, bromobenzene, and cupric chloride in the requisite proportions.

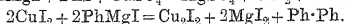
The anhydrous cupric chloride used was either the commercial preparation or that obtained by dehydrating the hydrated salt at 100°.

Anhydrous cupric sulphate reacts slowly with magnesium phenyl iodide, cupric iodide apparently being formed as an intermediate compound. It is hoped that this will ultimately lead to the preparation of cupric iodide. The reactions summed up by the equation



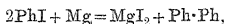
however, only proceed with difficulty, partly owing, no doubt, to the very sparing solubility of the anhydrous salt in ether.

In the presence of iodobenzene, a steady reaction occurs, probably according to the equations



Thus when anhydrous cupric sulphate (1 mol.) is added to an ethereal solution of magnesium (2 atoms) and iodobenzene (3 mols.), a 65—70 per cent. yield of diphenyl is obtained.

Comparative experiments showed that the diphenyl produced was due neither to initial interaction of the magnesium and iodobenzene,



nor to interaction between magnesium phenyl iodide and iodobenzene,



The reactivity of cupric sulphate with magnesium phenyl iodide seems to depend on the instability of the cupric iodide formed. Magnesium phenyl bromide does not react with cupric sulphate under similar conditions.

## EXPERIMENTAL.

### *Action of Anhydrous Cupric Chloride on Magnesium Phenyl Bromide.*

Magnesium turnings (4.9 grams) were covered with 150 c.c. of pure ether, 28 grams of anhydrous cupric chloride and then 32 grams of bromobenzene were added, and the mixture was well shaken. A vigorous reaction set in, and was controlled, when necessary, by shaking and external cooling. When the initial reaction had subsided, the mixture was heated under reflux in warm water for two hours, cooled, decomposed with ice and water, and treated with excess of concentrated hydrochloric acid in order to redissolve the precipitated cuprous chloride. The ethereal layer was separated, and the aqueous layer extracted repeatedly with ether. The united ethereal extracts were shaken with water to



precipitate the cuprous chloride remaining dissolved in the acidic ethereal solution, dried, and the solvent evaporated. Thirteen grams (that is, about 85 per cent. of the theoretical) of pure diphenyl were obtained.

Using 100 c.c., and 55 c.c. of ether instead of the 150 c.c. used above, yields of 65 and 50 per cent., respectively, were obtained. An increase in the volume of ether to 200 c.c. was not found to be advantageous.

*Interaction of Iodobenzene and Magnesium Phenyl Iodide.*

Magnesium (4.9 grams), iodobenzene (41 grams), and ether (200 c.c.) were converted into the Grignard reagent, which was treated with 41 grams of iodobenzene, and the mixture heated under reflux for several hours. The product, on decomposition, gave 2.5 grams of diphenyl, half the iodobenzene used being recovered unchanged.

*Interaction of Anhydrous Cupric Sulphate and Magnesium Phenyl Iodide.*

Anhydrous cupric sulphate (32 grams) was added to the Grignard reagent, prepared from 41 grams of iodobenzene, 4.9 grams of magnesium, and 200 c.c. of ether, the mixture boiled for six hours under reflux, and then left overnight. On working up the product, 6 grams of diphenyl were obtained, corresponding with a 39 per cent. yield on the iodobenzene used.

*Interaction of Cupric Sulphate (1 mol.), Magnesium (2 atoms), and Iodobenzene (3 mols.) in Ethereal Solution.*

Magnesium turnings (4.9 grams) were dissolved in 200 c.c. of pure ether in the presence of 62 grams of iodobenzene, and to the clear solution 16 grams of anhydrous cupric sulphate were added. The mixture was then boiled for three hours under reflux, cooled, decomposed with ice, and the solution obtained after acidifying extracted with ether, and so on. Sixteen grams of pure diphenyl were isolated, corresponding with a 66 per cent. yield on the iodobenzene used.

## OBITUARY NOTICE.

EDWARD FRANK HARRISON.

BORN JULY, 1869; DIED NOVEMBER 4TH, 1917.

EDWARD FRANK HARRISON was educated at the United Westminster Schools, and in 1884 was apprenticed to a pharmaceutical chemist in North London. In 1890 he gained the Bell scholarship of the Pharmaceutical Society, and proceeded to its school in Bloomsbury Square. There he was awarded medals and certificates in chemistry, botany, and materia medica, and after passing the minor and major examinations he occupied several positions on the staff, and carried out research on the alkaloids of aconite. While acting afterwards for five years with the firm of Messrs. Brady and Martin at Newcastle, he successfully used his leisure to prepare for the B.Sc. degree of London University. The next six years were spent as head of the analytical department of Messrs. Burroughs Wellcome and Co. In 1905 he went into partnership in a school of pharmacy, but finally took up the independent practice of consulting and analytical chemistry. He was an eminent specialist in the analysis of drugs and medicinal substances, and as analyst to the British Medical Association made nearly all the analyses of proprietary articles which were revealed in the two publications "Secret Remedies" and "More Secret Remedies."

In the Parliamentary inquiry which followed these disclosures, Harrison was a most important witness and made a deep impression on the Select Committee. The full value of this work to public health and public economy has yet to be realised.

Col. Harrison was a Fellow of the Institute of Chemistry, and published a number of papers on his special province of the science. His process for estimating the diastatic strength of malts is now in general use. He was active both as a student and a past student in the life of the Pharmaceutical Society's School, in which he was most highly regarded, and to which as his *alma mater* he was loyally devoted. He was a member of the board of examiners, and in 1917 he delivered a thoughtful and valuable address at the inauguration of the session. For three years he conducted the practical chemistry competitions maintained in the weekly

*Pharmaceutical Journal*. His professional life was, indeed, in the highest degree strenuous.

As soon as the War broke out Harrison was impatient to join the forces. After being refused several times on the ground of age, he became a special constable and a volunteer in the Inns of Court Reserve Corps. Later he succeeded in entering as a private in the Sportsmen's Battalion of the Royal Fusiliers. It was by an accident that he came under the notice of the first head of the anti-gas service at home, Col. Sir W. H. Horrocks, R.A.M.C., who with some difficulty succeeded in securing his services. He was given the rank of lieutenant on the general list in July, 1915, and from that time devoted himself to the anti-gas service. It was only in the last year that his duties extended over both branches of the gas service.

He was promoted major in April, 1916; lieutenant-col. in January, 1917. He was appointed Assistant Controller of Chemical Warfare in November, 1917; shortly before his death, his succession to Major-General Thuillier as Controller of Chemical Warfare had been settled, and in a few days he would have attained the rank of brigadier-general.

Harrison's work for the war may be considered as falling into two periods. In the first period, extending from the spring of 1915 until November of 1916, he was engaged in research work in the anti-gas laboratories at the Royal Army Medical College, Millbank, the chief subjects being the improvement of the anti-gas helmet, the devising of, first, the large, and then the small box respirator.

In the early part of this period Harrison was constantly in the laboratory, working late into the night. He realised from the first the critical importance of speed and the possession of the initiative, and up to the last he never relaxed the pace. It is not easy to give an idea of the range of problems, their variety and complexity, that had to be overcome in bringing to a state of service efficiency such simple-looking appliances as the helmet and box respirator. The mechanical, chemical, physiological, and, one may add, even psychological questions raised were innumerable. Many heads and hands contributed to achieve the success that ensued. The apportionment of credit does not arise here, but there can be little doubt that all concerned would agree in giving Harrison a foremost place. With his scientific knowledge were united a strong practical instinct and intuitive judgment, which enabled him to seize quickly the essence of a problem and the substance of a suggestion, and to preserve a splendid sense of proportion. He improved the formula for the impregnating fluid

of the helmet, and worked out laboratory tests for controlling its component materials and for testing its efficiency. He made numerous experiments, in which he fearlessly wore the helmet in gases for which suitable quantitative control tests had not then been devised. During the late summer and autumn of 1915, he was occupied chiefly in getting out the large box respirator. As is generally known, this appliance was based on the admirable suggestion by Bertram Lambert, of Oxford, of a filter of permanganate-soda-lime granules. The realisation of this plan in the form of a box which in itself and its contents should be serviceable under field conditions was a most difficult undertaking. By the end of the year it was completed, and an issue was made early in 1916. The production in large quantities at a time when a high grade of protection was becoming indispensable for troops in special situations was a great achievement, and the large box was in its chief essentials the prototype of the small box which not long after became and remained the standard protection for troops of all arms. For the design of the small box, the members of the Gas Service in France were able to make valuable suggestions based on field experience with the large box. Harrison also made many contributions based on his own practical trials.

During the second period of his work, Harrison was closely associated with Col. Sir W. H. Horrocks in the rapid organisation and development of factories for the manufacture of respirators. Though this withdrew him for the greater part of his time from the laboratory, he remained in close touch with it, and at the weekly meeting of senior officers his genius for improvisation, his sound chemical judgment, and his foresight as to profitable lines of work were constantly evident. It was at this period that the manufacture of a new type of granule and of absorptive charcoal was worked out in the laboratories and transferred under the direction of selected officers to manufacturing establishments. In the choice of officers, Harrison's judgment rarely led him astray, and his knack of getting the right men into the right place contributed largely to the success of all his work. The great success of the small box respirator and its remarkable freedom from faults were due in no small measure to the organisation of inspecting officers, on which Harrison laid great stress. Harrison was held in high esteem by the officers of the Gas Services of our French, Italian, and American Allies. He was received with great cordiality at their councils, and his opinion was eagerly sought. It may be remarked, as affording a tribute to the excellence of the British respirator, that the Italians were supplied with several millions, and that the Americans, besides taking large numbers,

paid us the compliment of copying it as soon as the home manufacture could be arranged. The French considered that the protection it gave was even unnecessarily high.

In the last year of his life Harrison was called on to participate in the offensive side of gas warfare, and to exercise his great organising talent in what had become a very imposing and difficult undertaking. He had now reached the position to which his talents and labours so justly entitled him, but before he could actually officiate as Director of Chemical Warfare, the haunting fear of his friends was realised, and he was prostrated by influenza. His bodily strength, sapped by unceasing labour, was unequal to the strain, pneumonia supervened, and he passed away, as certainly as anyone on the battlefield, a sacrifice of the war. His elder son had fallen in France in 1916.

It is not easy to do justice to Harrison's personal qualities. He was a man of the strongest character. The love of his country, its ideals of freedom, its democratic institutions, and his belief in the destiny of the British as leaders among free peoples were the inspiration of his life and work. He had no thought for himself when the lives of others were at stake. The inflexible sense of duty which animated him communicated itself to those who worked with him, and he gained in a remarkable degree their respect and affection. He faced all emergencies with imperturbability, was never daunted or discouraged, and preserved a clear head and a power of decision even when worn out with incessant labour. He was neither dogmatic nor impatient, but always ready to improve on himself, listening with patience and courtesy to all honest criticism or advice. He was a master organiser, and the War brought him his opportunity. He died acknowledged and revered as a leader of men, his great task accomplished. He was buried with full military honours, mourned by a multitude of fellow-labourers who had learned something of his worth.

Harrison died before he had received the public honours that would undoubtedly have been conferred on him. He had been made C.M.G. in 1917, and the French had shown their appreciation of his services by making him Officer of the Legion of Honour. It is gratifying to know that a memorial to perpetuate his name is to be associated with the Chemical Society. What the nation owes him for the saving of life and the mitigation of suffering can scarcely be overestimated.

A. S.  
H. S. R.

*XLV.—Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part I. Position-Isomerism and Optical Activity of Naphthyliminocamphors and Derivatives of Phenyliminocamphor.*

By BAWA KARTAR SINGH and JATINDRA KUMAR MAZUMDER.

THE relation between chemical constitution and rotatory power which is investigated in the present paper is that of position-isomerism in the aromatic groups present in optically active derivatives of phenyliminocamphor.

Frankland in 1896 (T., 69, 1583) suggested a theory to explain the changes in rotatory power produced by nuclear substitution in the ortho-, meta-, and para-position in a side-chain containing an active group.

Taking the analogy of a weight acting at the end of a lever arm, he suggested, for reasons based on the relative position of the centre of gravity of the unsubstituted aromatic nucleus on the one hand, and those of the isomeric disubstituted derivatives on the other, that the order of rotatory power should be:

Ortho < unsubstituted nucleus < meta < para.

The line of argument adopted was as follows:

The centre of gravity of the unsubstituted nucleus being at the centre of a regular hexagon, that in the ortho-substituted derivative would be somewhat nearer, in the meta-derivative somewhat further, and in the para-derivative still further than that geometrical centre from the side-chain containing the optically active group.

If, then, the optical activity is determined by the moment of the mass of the group, the rotatory power of the para-compound should be the greatest, that of the ortho-compound the least, and that of the meta-derivative intermediate between those of the other two. In the case of the unsubstituted nucleus, the mass is smaller, but it acts through a longer arm than in the case of the larger mass of the ortho-compound, but through a shorter arm than in either the meta- or the para-compound.

In his Presidential Address to the Chemical Society (T., 1912, 101, 654), Frankland revived this theory, and illustrated its validity by several observations of Cohen and his collaborators. A number of other observations (Cohen, T., 1903, 83, 1214;

T., 1904, **85**, 1271; T., 1905, **87**, 1190; T., 1911, **99**, 1058), however, do not support the rule.

The aim of the present work is to afford evidence in support or in refutation of Frankland's rule from observations made in several series of new compounds. If the theory were correct, that is, if the rotatory power were determined by the position of the centre of gravity of the nucleus in relation to the active group, we should expect: (1) that the greater the mass of the substituting group or element, the greater would be the observed differences between the constants of the para- and ortho-isomerides, and (2) that the para-isomeride would have the maximum rotation.

The molecular rotatory powers of derivatives of phenyliminocamphor are tabulated below.

TABLE I.

Derivatives of phenyliminocamphor.	[M] <sub>D</sub> in chloroform solution.			
	-CH <sub>3</sub> (15)	-Br(80)	-Cl(35.5)	-O-CH <sub>3</sub> (31)
Ortho-	+1183°	+1382°	+441.7°	+612°
Meta-	1665	1338	1338	—
Para-	2177	1695	1768 (a)	3314 (a)

The value of [M]<sub>D</sub> of phenyliminocamphor is 1750° (Forster and Thornley, T., 1909, **95**, 944).

TABLE II.

Derivatives of phenylimino- camphor.	[M] <sub>D</sub> in methyl alcohol.		
	-CH <sub>3</sub> (15)	-Br(80)	-Cl(35.5)
Ortho-	+1030°	+1311°	+486.4°
Meta-	1504	1260	1261
Para-	2001	1545	—

The value of [M]<sub>D</sub> for phenyliminocamphor in methyl alcohol solution is 1462°.

The mean temperature of observations recorded in tables I and II was 26° to 32°.

It will now be seen that in no case is Frankland's rule borne out by the results recorded in tables I and II. In the case of the tolyl and chlorophenyl derivatives, the value of the rotatory power for the unsubstituted compound (namely, phenyliminocamphor) lies between that for the meta- and para-derivative, and is therefore in opposition to Frankland's rule. The order of rotatory powers in the case of the bromophenyl derivatives in chloroform is meta < ortho < para < unsubstituted compound, and here deviation from Frankland's rule is seen to be most marked.

Although the mass of the group ( $\text{CH}_3$ ) in the case of the tolyl compounds is less than that in the case of the bromophenyl derivatives (Br), the observed difference in the values of the rotatory powers of the ortho- and para-isomerides is more than three times as high in the former as in the case of the latter. This result is again contrary to what we should expect if Frankland's rule were valid.

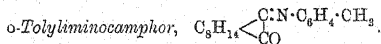
The para-isomeride has in all the above cases, except in the case of the bromophenyl derivative, the maximum rotation, and this is in accordance with the deduction made from Frankland's rule.

It is thus clear that the results recorded in the present paper do not generally support Frankland's rule. Only in one direction can we say that Frankland's theory has been supported, namely, that the ortho-compound has the least and the para-derivative the maximum rotation (except in one instance).

Cohen, as the result of his observations (T., 1910, 97, 1737; 1911, 99, 1060), lays down the following rule: The rotatory effect of the ortho-grouping differs more from that of the phenyl than do those of meta- and para-groupings. A glance at tables I and II will show that this rule is also not supported. In the case of the bromophenyl derivatives, it is the meta, and in the case of the methoxyphenyl derivatives it is the para, and not the ortho, which differs more in rotation from the value of the unsubstituted compound.

Further, no simple connexion can be observed between the nature of the substituting element or group in an optically active compound and its rotatory power. In the case of ortho-compounds (table I), it is seen that the order of elements or groups with increasing rotation is  $\text{Cl} < \text{O}\cdot\text{CH}_3 < \text{CH}_3 < \text{Br} < \text{H}$ , in the case of meta-compounds  $\text{Cl} = \text{Br} < \text{CH}_3 < \text{H}$ , and in the case of para-compounds  $\text{Br} < \text{H} < \text{Cl} < \text{CH}_3 < \text{O}\cdot\text{CH}_3$ .

#### EXPERIMENTAL.



Camphorquinone and *o*-toluidine in molecular proportion were heated with anhydrous sodium sulphate for several hours on the water-bath. On cooling, water was added, when a solid substance was precipitated, which crystallised from 50 per cent. alcohol in yellow prisms melting at 120—121°.

It is very readily soluble in chloroform, ether, benzene, or acetone, less so in methyl or ethyl alcohol, and insoluble in water:



0.2074 gave 10.6 c.c.  $N_2$  at  $30^\circ$  and 759.5 mm.  $N=5.78$ .

$C_{17}H_{21}ON$  requires  $N=5.49$  per cent.

The following determinations of rotatory power were made by dissolving the given weight of substance in 19.9 c.c. of the solvent, and the first observation was made within half an hour of making up the solution. This applies to all the observations, unless the contrary is stated. The length of the tube was 2-dcm.

Solvent.	Substance. Gram.	Tem- perature.	Time hours.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
Chloroform .....	0.1470	$32^\circ$	—	+6.85°	+464.1°	+1183°
.....	.....	.....	19	6.86	464.4	1184
Methyl alcohol.....	0.1519	$34^\circ$	—	6.16	403.6	1030
„ .....	„	„	21	6.08	398.4	1016

*m-Tolyliminocamphor.*

Molecular proportions of camphorquinone and *m*-toluidine, mixed with a little fused sodium sulphate, were heated on the water-bath for five hours. The product was cooled and dissolved in a small quantity of alcohol; water was added, when an oil separated which solidified on keeping. The substance was crystallised from dilute (50 per cent.) alcohol in yellow prisms melting at  $85-86^\circ$ .

It is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water:

0.1425 gave 7.6 c.c.  $N_2$  at  $31^\circ$  and 760 mm.  $N=5.9$ .

$C_{17}H_{21}ON$  requires  $N=5.49$  per cent.

The rotatory power determinations gave the following values:

	Solvent.	Substance. Gram.	Tem- perature.	Time in hours.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
(a)	Chloroform ...	0.0649	$31^\circ$	—	+4.26°	+653.0°	+1665°
	„ ...	„	$29.5^\circ$	20	4.31	660.7	1684
(b)	„ ...	0.0915	$17-18^\circ$	—	6.04	656.7	1675
	Methyl alcohol	0.0903	$31.0^\circ$	—	5.35	589.7	1504
	„	„	$29.5^\circ$	$13\frac{1}{2}$	5.35	589.7	1504

*p-Tolyliminocamphor.*

An alcoholic solution of camphorquinone was mixed with a similar solution of *p*-toluidine (in molecular proportion), a little anhydrous sodium sulphate added, and the solution was heated on the water-bath under reflux for three hours. After evaporating off the alcohol, the residue was poured into water, when a yellow substance separated, which crystallised from dilute alcohol (50 per cent.) in yellow prisms melting at  $121-122^\circ$ . It is very readily soluble in chloroform, acetone, ether, or benzene, less so in methyl or ethyl alcohol, and insoluble in water:

0.2118 gave 10.6 c.c.  $N_2$  at  $29^\circ$  and 764 mm.  $N=5.71$ .

$C_{17}H_{21}ON$  requires  $N=5.49$  per cent.

The rotatory power determinations gave the following values :

Solvent.	Substance. Gram.	Tem- perature.	Time in hours.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
Chloroform .....	0.1691	$28.0^\circ$	—	+14.51°	+853.9°	+2177°
Methyl alcohol.....	0.1583	$29.0^\circ$	—	12.48	784.5	2001
" .....	"	$29.0^\circ$	48	11.95	694.5	1771
" .....	"	$30.5^\circ$	76	10.2	641.1	1634.8
" .....	"	$29.5^\circ$	142	8.79	552.6	1409
" .....	"	$30.5^\circ$	166	8.26	519.2	1324
" .....	"	$30.0^\circ$	219	7.55	474.5	1210

The substance when recovered from the polarimeter tube by evaporation to dryness on the water-bath melts at about  $110^\circ$ .



Camphorquinone was added to the calculated quantity of *o*-bromoaniline and a little anhydrous sodium sulphate, the mixture being heated on the water-bath for five hours, cooled, and then dissolved in alcohol. The alcoholic solution on dilution with water furnished an oil, which became solid on keeping for two or three days, and crystallised from dilute alcohol (50 per cent.) in yellow needles melting at  $110^\circ$ .

It is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water :

0.1109 gave 4.6 c.c.  $N_2$  at  $33^\circ$  and 761 mm.  $N=4.65$ .

$C_{16}H_{18}ONBr$  requires  $N=4.4$  per cent.

The rotatory power determinations gave the following values :

Solvent.	Substance. Gram.	Tem- perature.	Time in hours.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
Chloroform .....	0.0380	$32.0^\circ$	—	+1.65°	+432.1°	+1382°
" .....	"	$31.0^\circ$	14½	1.64	429.4	1374
Methyl alcohol.....	0.0362	$31.0^\circ$	—	1.49	409.6	1311
" .....	"	$31.5^\circ$	20½	1.19	327.2	1047

*m*-Bromophenyliminocamphor.

Camphorquinone and *m*-bromoaniline were heated together in the presence of a little anhydrous sodium sulphate on the water-bath for four hours. On cooling, the product was dissolved in alcohol and precipitated by the addition of water. It crystallised from dilute alcohol (50 per cent.) in yellow prisms melting at  $116\text{--}118^\circ$ , which were very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water :

0.1085 gave 0.0638 AgBr. Br=25.0.

$C_{16}H_{18}ONBr$  requires Br=25.0 per cent.

The rotatory power determinations gave the following values:

Solvent.	Substance. Gram.	Tem- perature.	Time in hours.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
Chloroform .....	0.1392	31°	—	+5.85°	+418.3°	+1338°
.....	.....	31	7½	5.81	415.5	1329
Methyl alcohol.....	0.1461	31	—	5.78	393.9	1260
.....	.....	31	5	5.52	376.2	1204
.....	.....	31	22	4.94	336.7	1077

The substance when recovered from methyl-alcoholic solution after the last observation by evaporating to dryness on the water-bath melted at 113—114°. A mixture with the original substance melted at 116—118°. It is therefore obvious that the substance undergoes mutarotation in methyl-alcoholic solution, and not in chloroform solution.

*p*-Bromophenyliminocamphor.

Camphorquinone and *p*-bromoaniline were mixed together in equal quantities. The reaction began at the ordinary temperature, as the mixture became liquid within a short time. After heating for four hours on the water-bath, the reaction was complete. On cooling, the product solidified, and crystallised from dilute alcohol (50 per cent.) in yellow needles melting at 138—139°. The substance is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water:

0.0750 gave 3.2 c.c.  $N_2$  at 35° and 759 mm. N=4.74.

$C_{16}H_{18}ONBr$  requires N=4.4 per cent.

The rotatory power determinations gave the following values:

Solvent.	Substance. Gram.	Tem- perature.	Time in hours.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
Chloroform .....	0.1217	31°	—	+6.48°	+529.9°	+1695°
.....	.....	30	20	6.53	534.0	1709
Methyl alcohol.....	0.1193	31	—	5.79	483.0	1545
.....	.....	30	22	4.31	359.5	1150
.....	.....	30	46	3.36	280.2	896.6

The substance when recovered from methyl-alcoholic solution after the last observation, by evaporation to dryness, melted at 112—118°, a mixture with the original substance melting at 115—122°. It is clear that the substance exhibits mutarotation in methyl alcohol, but not in chloroform.



Camphorquinone and *o*-chloroaniline were condensed with the aid of a little sodium sulphate by heating on the water-bath for five hours. On allowing to cool, the substance solidified, and crystallised from dilute alcohol (50 per cent.) in silky, yellow needles melting at 128°.

It is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, but sparingly so in water:

0.1233 gave 5.6 c.c.  $\text{N}_2$  at 28° and 758 mm.  $\text{N}=5.16$ .

$\text{C}_{16}\text{H}_{18}\text{ONCl}$  requires  $\text{N}=5.1$  per cent.

The rotatory power determinations gave the following values:

Solvent.	Substance. Gram.	Tem- perature.	Time in hours.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
(a) Chloroform ...	0.0633	27.5°	—	+1.02°	+160.4°	+441.7°
" ...	"	28.0	8	1.03	161.9	446.0
(b) " ...	0.0994	30.0	—	1.54	154.1	424.6
	(2nd prepn.)					
" ...	"	31.0	7½	1.54	154.1	424.6
Methyl alcohol	0.0941	30.0	—	1.67	176.6	486.4
"	"	31.0	6½	1.67	176.6	486.6

*m*-Chlorophenyliminocamphor.

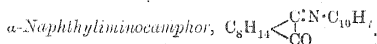
Molecular proportions of camphorquinone and *m*-chloroaniline were condensed with the aid of anhydrous sodium sulphate by heating on the water-bath for four hours. The product was cooled, dissolved in alcohol, and precipitated by the addition of water as a crystalline substance. On recrystallisation from dilute alcohol, pale yellow needles melting at 123—124° were obtained. The substance is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water:

0.1300 gave 6.2 c.c.  $\text{N}_2$  at 32° and 758 mm.  $\text{N}=5.35$ .

$\text{C}_{16}\text{H}_{18}\text{ONCl}$  requires  $\text{N}=5.1$  per cent.

The rotatory power determinations gave the following values:

Solvent.	Substance. Gram.	Tem- perature.	Time in hours.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
Chloroform .....	0.0666	28.0°	—	+3.25°	+485.7°	+1338°
" .....	"	27.5	24	3.19	476.7	1313
Methyl alcohol .....	0.0800	27.5	—	3.68	457.7	1261
" .....	"	26.5	20	3.69	459.0	1264



When molecular proportions of camphorquinone and  $\alpha$ -naphthylamine were mixed, the mixture soon became liquid at the ordinary temperature. It was heated on the water-bath for four hours to complete the reaction. On cooling, the product was dissolved in alcohol and precipitated by the addition of water, when a solid substance separated which crystallised from dilute alcohol in yellow needles melting at  $155^\circ$ .

It is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water:

0.1220 gave 5.1 c.c.  $\text{N}_2$  at  $33^\circ$  and 759 mm.  $\text{N} = 4.7$ .

$\text{C}_{20}\text{H}_{21}\text{ON}$  requires  $\text{N} = 4.8$  per cent.

The rotatory power determinations gave the following values:

Solvent.	Substance. Gram.	Tem- perature.	Time in hours.	$\alpha_D$ .	$[\alpha]_D$ .	$[\text{M}]_D$ .
Chloroform .....	0.0676	$31.5^\circ$	—	$+4.14^\circ$	$+609.6^\circ$	$+1774^\circ$
		32.0	$9\frac{1}{2}$	4.14	609.6	1774
Methyl alcohol.....	0.1199	31.5	—	6.73	558.5	1625
		32.0	$7\frac{1}{2}$	6.73	558.5	1625

The substance does not exhibit any mutarotation.

#### *$\beta$ -Naphthyliminocamphor.*

Camphorquinone and  $\beta$ -naphthylamine were condensed in molecular proportions by heating on the water-bath for four hours. The substance on crystallisation from dilute alcohol in the usual manner gave yellow needles melting at  $140\text{--}142^\circ$ .

These are very readily soluble in methyl or ethyl alcohol, acetic acid, ether, or chloroform, and insoluble in water:

0.1100 gave 4.6 c.c.  $\text{N}_2$  at  $32^\circ$  and 760 mm.  $\text{N} = 4.4$ .

$\text{C}_{20}\text{H}_{21}\text{ON}$  requires  $\text{N} = 4.8$  per cent.

The rotatory power determinations gave the following values:

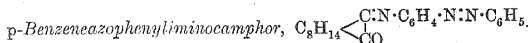
Solvent.	Substance. Gram.	Tem- perature.	Time in hours.	$\alpha_D$ .	$[\alpha]_D$ .	$[\text{M}]_D$ .
Chloroform .....	0.0966	$32^\circ$	—	$+6.62^\circ$	$+682.0^\circ$	$+1985^\circ$
		31	15	6.66	686.0	1996
Methyl alcohol.....	0.1140	31	—	7.45	650.5	1893
		31	$10\frac{1}{2}$	7.35	641.6	1867

#### *Phenyliminocamphor.*

This substance was prepared according to Forster's method (T., 1909, 95, 949), and formed silky, yellow needles melting at  $110\text{--}112^\circ$ .

The rotatory power determinations gave the following values :

Solvent.	Substance. Gram.	Tem- perature.	Time in hours.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
Methyl alcohol.....	0.0920	26.5°	—	+5.61°	+606.8°	+1462°
„ .....	„	27.0	27	5.51	596.1	1437



Camphorquinone and aminoazobenzene, in molecular proportions, were heated on the water-bath for six hours. The product was cooled, dissolved in alcohol, and precipitated as an oil by the addition of water. The oil, on keeping for two days, solidified. It crystallised from dilute alcohol in orange needles melting and decomposing at 129—130°.

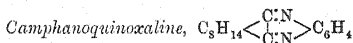
The substance is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water :

0.1140 gave 12.5 c.c.  $N_2$  at 32° and 759 mm.  $N=12.5$ .

$C_{22}H_{23}ON_3$  requires  $N=12.36$  per cent.

The rotatory power determinations gave the following values :

Solvent.	Substance. Gram.	Tem- perature.	Time in hours.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
Chloroform .....	0.0557	23.0°	—	+3.08°	+550.4°	+1899°
„ .....	„	23.5	22	3.25	530.8	2004
Methyl alcohol.....	0.0359	24.0	—	2.06	571.1	1970
„ .....	„	24.5	22	2.05	568.4	1961



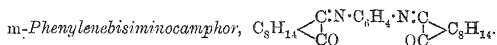
The quinoxaline derivative is obtained quantitatively by heating on the water-bath alcoholic solutions of camphorquinone and *o*-phenylenediamine. On dilution with water, it separates as an oil, which on rubbing becomes pasty and then solidifies. It is purified by dissolving in alcohol and precipitating with water, being obtained as a white, amorphous substance melting at 77—78°. It is very readily soluble in methyl or ethyl alcohol, acetone, glacial acetic acid, ether, benzene, light petroleum, carbon disulphide, or chloroform, and insoluble in water :

0.1725 gave 18.55 c.c.  $N_2$  at 30.5° and 759.5 mm.  $N=12.1$ .

$C_{16}H_{18}N_2$  requires  $N=11.76$  per cent.

The rotatory power determinations gave the following values :

Solvent.	Substance. Gram.	Tem- perature.	Time in hours.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
Ethyl alcohol .....	0.2980	23.5°	—	+0.97°	+32.4°	+77.1°
" .....	"	24.0	8½	0.94	31.4	74.71
" .....	"	23.0	23½	0.94	31.4	74.71
Chloroform .....	0.3979	28.0	—	1.14	28.51	67.86
" .....	"	27.0	18	1.17	29.26	69.65
Methyl alcohol.....	0.4254	30.0	—	1.43	33.45	79.6



An alcoholic solution of camphorquinone (2 mols.) was added to an aqueous solution of *m*-phenylenediamine hydrochloride mixed with excess of sodium acetate, and heated for half an hour on the water-bath. The condensation product was obtained as an oil, which solidified on keeping and crystallised from dilute alcohol in yellow needles melting at 150—151°.

It is very readily soluble in methyl or ethyl alcohol, acetic acid, chloroform, ether, or pyridine, and insoluble in water:

0.1300 gave 8.25 c.c.  $\text{N}_2$  at 31° and 760 mm.  $\text{N}=7.16$ .

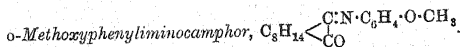
$\text{C}_{26}\text{H}_{32}\text{O}_2\text{N}_2$  requires  $\text{N}=6.93$  per cent.

The same substance was also obtained when camphorquinone and *m*-phenylenediamine were condensed in molecular proportions.

The rotatory power determinations gave the following values:

Solvent.	Substance. Gram.	Tem- perature.	Time in hours.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
Methyl alcohol.....	0.0193	30.5°	—	+1.23°	+634.1°	+2563°
Chloroform .....	0.0395	29.0	—	0.52	658.3	2660
" .....	(in 100 c.c.)	28.0	21	0.53	671.0	2710

More concentrated solutions were too dark for observations to be made on them.



Camphorquinone and *o*-anisidine were mixed in molecular proportions, a little anhydrous sodium sulphate was added, and the whole heated on the water-bath for four hours. On cooling the product, it was dissolved in alcohol and precipitated by water. It crystallised from dilute alcohol in pale yellow prisms melting at 125—126°.

The substance is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water:

0.1135 gave 5.6 c.c.  $\text{N}_2$  at 28° and 759 mm.  $\text{N}=5.61$ .

$\text{C}_{17}\text{H}_{21}\text{O}_2\text{N}$  requires  $\text{N}=5.2$  per cent.

The rotatory power determinations gave the following values. The solution was somewhat dark, and therefore difficult to read:

Solvent.	Substance. Gram.	Tem- perature.	Time in hours.	$\alpha_d$ .	$[\alpha]_D$ .	$[M]_D$ .
Chloroform .....	0.0639	27°	—	+1.45°	+225.8°	+612.0°
" .....	"	28	27	1.47	228.9	620.3

Condensations between camphorquinone and *m*-nitro-*p*-toluidine, *o*-, *m*-, and *p*-aminobenzoic acids, could not be effected.

This work was carried out at Dacca College. It is now being continued at Government College, Lahore.

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[Received, January 13th, 1919.]

## XLVI.—The Nitration of Diphenylethylenediamine.

By GEORGE MACDONALD BENNETT.

It was shown by Mills in 1900 (T., 77, 1020) that diphenylethylenediamine,  $C_6H_5 \cdot NH \cdot CH_2 \cdot CH_2 \cdot NH \cdot C_6H_5$ , may be nitrated in glacial acetic acid solution with the production of two isomeric tetranitro-derivatives, one melting at 303°, the other at 85°, the latter being much the more readily soluble in various solvents, and easily converted into the former by boiling its solution in acetone.

The close relationship between diphenylethylenediamine and monomethylaniline made it probable that an octanitro-derivative of the former might be obtained, analogous to trinitrophenylmethylnitroamine,  $C_6H_2(NO_2)_3 \cdot NMe \cdot NO_2$ . This proved to be the case, and the expected hexanitrodiphenylethylenedinitroamine,  $[C_6H_2(NO_2)_3 \cdot N(NO_2) \cdot CH_2]_2$ , was isolated, either by nitrating the base in sulphuric acid, using a large excess of fuming nitric acid, or by using little more than the theoretical amount of nitric acid in the presence of fuming sulphuric acid.

From the products of the reaction there was also isolated a small quantity of a hexanitro-derivative, which must be isomeric with the compound melting at 230° obtained by Jedlicka (*J. pr. Chem.*, 1893, [ii], 48, 204) by the interaction of ethylenediamine and either trinitroanisole or picryl chloride. This new hexanitrodiphenylethylenediamine and the Mills's tetranitro-compound (m. p. 85°), which it resembles closely in properties, are probably tetra- and di-nitrodiphenylethylenedinitroamines.



## EXPERIMENTAL.

*Preparation of Diphenylethylenediamine.*

The base has hitherto been prepared by the interaction of aniline and ethylene dibromide (Morley, *Ber.*, 1879, 12, 1794), but it may be equally readily obtained by using the dichloride, the mixture of the latter with four molecular proportions of aniline being boiled for three-quarters of an hour. The reaction is much less violent than with the bromide. The base may be conveniently purified in the form of its *sulphate*,  $C_{14}H_{16}N_2 \cdot H_2SO_4 \cdot H_2O$ , which crystallises from hot water in colourless needles, being sparingly soluble in the cold:

1.502 (air-dried) lost in a vacuum 0.079.  $H_2O = 5.3$ .

$C_{14}H_{16}N_2 \cdot H_2SO_4 \cdot H_2O$  requires  $H_2O = 5.8$  per cent.

0.3914 required 23.98 c.c.  $N/10-NaOH$ . Calc., 23.86 c.c.

*2:4:6:2':4':6'-Hexanitrodiphenylethylenedinitroamine.*

Fifteen grams of the sulphate (dried at  $110^\circ$ ) were dissolved in 100 grams of sulphuric acid (97 per cent.), and the solution was run slowly into 60 c.c. of fuming nitric acid (D 1.52) kept vigorously stirred at  $30-35^\circ$ . The temperature of the mixture was then slowly raised, and kept finally at  $80^\circ$  during an hour. When the product was cold, the solid which had been precipitated was collected on asbestos and washed successively with dilute sulphuric acid (70 per cent.), water, sodium carbonate solution, and finally with water. There remained, after drying, 19 grams of a yellow, sandy powder which melted and decomposed at  $200^\circ$ . A similar result was obtained when the nitration was carried out in the presence of fuming sulphuric acid, using the calculated amount\* (eight molecular proportions) of nitric acid. By washing the sandy product with ethyl acetate or, better, by recrystallisation from acetone, in which it is sparingly soluble, the octanitro-derivative was obtained as a pale yellow, crystalline powder melting and decomposing at  $213^\circ$  (uncorr.):

0.2771 gave 0.2974  $CO_2$  and 0.0400  $H_2O$ .  $C = 29.3$ ;  $H = 1.61$ .

0.1315 „ 26.75 c.c.  $N_2$  (moist) at  $15^\circ$  and 763 mm.

$N = 24.03$ .

$C_{14}H_8O_{10}N_{10}$  requires  $C = 29.3$ ;  $H = 1.4$ ;  $N = 24.5$  per cent.

This compound is insoluble in the ordinary organic solvents, with the exception of ethyl acetate and acetone, in which it is appreciably soluble. It may be obtained in minute, lemon-yellow crystals

by crystallisation from nitrobenzene, in which it is readily soluble. It explodes on sudden heating. When heated with a concentrated solution of sodium hydroxide, it is decomposed, with the formation of picric acid.

*Hexanitro-derivative.*

The dark-coloured mother liquors from the purification of the crude octanitro-derivative by means of ethyl acetate or acetone left, on evaporation, a dark brown powder which appeared to be a mixture, and from which crystalline products could not readily be isolated. By fractional precipitation of its solution in glacial acetic acid by the addition of water, an amorphous, canary-yellow powder was obtained which melted and decomposed at  $70^{\circ}$ , and appeared to be a hexanitro-derivative:

0.1834 gave 0.2362  $\text{CO}_2$  and 0.0413  $\text{H}_2\text{O}$ .  $\text{C}=34.6$ ;  $\text{H}=2.5$ .

$\text{C}_{14}\text{H}_{10}\text{O}_{12}\text{N}_8$  requires  $\text{C}=34.8$ ;  $\text{H}=2.07$  per cent.

It is readily soluble in acetone, glacial acetic acid, ethyl acetate, or nitrobenzene, but practically insoluble in chloroform, benzene, carbon tetrachloride, or light petroleum.

This investigation was carried out during 1915 in the Cambridge University laboratories at the suggestion of Prof. Sir William Pope, to whom the author's best thanks are due.

50, CITY ROAD, E.C. 1.

[Received, May 2nd, 1919.]

## XLVII.—*The Propagation of Flame in Mixtures of Acetylene and Air.*

By WALTER MASON and RICHARD VERNON WHEELER.

MEASUREMENTS of the speed of the "uniform movement" during the horizontal propagation of flame in mixtures of acetylene and air have recently been made by Haward and Sastry (T., 1917, 111, 841) in revision of earlier determinations by Le Chatelier (*Compt. rend.*, 1895, 121, 1144).

The electrical method of measuring the speeds of the flames employed by Haward and Sastry was found by them to be unsatisfactory when the propagation took place in a tube of as large a diameter as 25 mm., the duration of the uniform movement being too short and its speed too great to allow of sufficiently

accurate records being obtained. For this reason, they reported only results procured by using a tube 12 mm. in diameter. The tube employed by Le Chatelier was 40 mm. in diameter.

The maximum speeds during the uniform movement were found to be with mixtures containing from 8 to 10 per cent. of acetylene, and were: in a 12-mm. tube (Haward and Sastry), 260 cm. per second; in a 40-mm. tube (Le Chatelier), about 600 cm. per second.

From the results obtained with inflammable gases other than acetylene (see, for example, T., 1917, 111, 1044), one would not expect to find the speed of the uniform movement of flame so dependent on the diameter as these figures indicate. Means were therefore sought to compare the speeds in tubes of different diameters. From the appearance of the flames, it seemed probable that they would have sufficient actinic power to affect a sensitive photographic film during quite a short time of exposure, so that it should be possible to employ the photographic method of recording the speeds of flames devised by Mallard and Le Chatelier (*Ann. des Mines*, 1883, [viii], 4, 312) for use with mixtures of carbon disulphide with oxygen or nitric oxide, the flames of which are highly actinic. On trial, it was found that over the whole range of inflammable mixtures of acetylene and air a sufficiently definite image of the flame was obtained on a highly sensitive photographic film moving at a rapid speed in a direction normal to the direction of propagation of flame.

This method, described in detail in the experimental portion of this paper, was therefore adopted for the determinations of the speeds of the uniform movement of flame in mixtures of acetylene and air herein recorded, tubes 12.5, 25, 50, and 90 mm. in diameter being used.

Apart from its value in enabling the mean speed of propagation of flame over a measured distance to be calculated, the photographic method enables a detailed study to be made of the manner of movement of the flame. Such a study has been made, with particular reference to the phenomena resulting in and accompanying the detonation wave, by Dixon (*Phil. Trans.*, 1903, [A], 200, 315), who has brought flame "analysis" by these means to the acme of perfection.

Mallard and Le Chatelier's observations on the mode of propagation of flame, as revealed by photographs, have frequently been epitomised; but it is desirable to recall them again, preferably in Le Chatelier's words, which are as follow ("Le Carbone," p. 273, Paris, 1908):

"On constate dans ces conditions, lorsque l'inflammation a été mise du côté de l'extrémité ouverte du tube, que la flamme se

propage d'abord avec une vitesse sensiblement uniforme; la courbe enregistrée est alors une droite, plus ou moins inclinée; il se développe bientôt des mouvements vibratoires dans la masse gazeuse qui prennent parfois une violence extraordinaire, la courbe présente des ondulations très accentuées; enfin, dans certains cas, la propagation de l'inflammation devient brusquement, en quelque sorte, instantanée, du moins tellement rapide qu'il est bien difficile de reconnaître l'existence d'une vitesse définie."

This description is founded mainly on the results of experiments with mixtures of carbon disulphide and nitric oxide, for with no other inflammable gas was the flame sufficiently rich in actinic rays to affect satisfactorily the rapidly moving sensitised paper (gelatino-bromide paper) which Mallard and Le Chatelier used. The description is, however, intended to apply to the propagation of flame in most gaseous mixtures ignited under the conditions specified.

It will be understood that an advantage of this method of determining the speed of uniform movement of flame, over such as involve the fusion of screen-wires at fixed positions along its path, lies in the assurance given by the photograph that no part of the "vibratory movement," during which the flame may momentarily attain a very rapid speed, is included in the measurement.

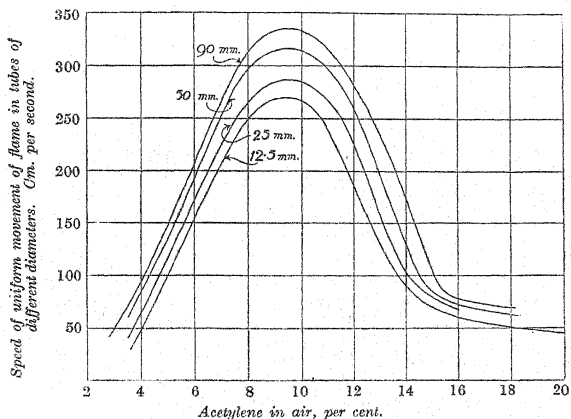
In the present instance, the necessity of avoiding the development of the detonation wave, with consequent shattering of the glass apparatus, demanded that tubes of not much greater length than 150 cm. should be employed. With such short tubes, the uniform movement may give place to the vibratory movement at a distance of less than 20 cm. from the point of ignition (the open end of the tube). It is difficult to record accurately the times of fusion, by rapidly moving flames, of screen-wires placed so close together as this.

There is little doubt but that the inadvertent inclusion of part of the vibratory movement of the flame in the measurement of the speed of the uniform movement has been responsible for some of the discrepant results reported by different experimenters. It would seem most probable that herein lies the explanation of the high velocities recorded by Le Chatelier for the uniform movement of flame in mixtures of acetylene and air in a tube of 40 mm. diameter; for whilst the photographic method of recording the speeds confirms the results obtained by Haward and Sastry when using a tube 12 mm. in diameter, neither in a 50 mm. nor even in a 90 mm. tube did the flames attain during the uniform movement such high speeds as in Le Chatelier's experiments. The maximum speed of flame shown by the photographs during the uniform

movement was 335 cm. per second, for mixtures containing between 9 and 10 per cent. of acetylene (tube 90 mm. in diameter); as compared with 600 cm. per second recorded by Le Chatelier for like mixtures (tube 40 mm. in diameter).

In Fig. 1 the results obtained in the four tubes of different diameters are plotted as speed-percentage curves. The influence of the diameter of the tube on the speed of the uniform movement of flame in mixtures of acetylene and air is shown by this diagram to be of the same degree as with other inflammable gases. For example, the maximum speeds may be compared with those for

FIG. 1.



mixtures of methane and air in tubes of the same diameters (T., 1917, 111, 1052), as follows:

Speed of uniform movement of flame.  
Cm. per sec.

Diameter of tube in mm.	Speed of uniform movement of flame. Cm. per sec.		Ratio.
	Methane-Air (9.5 per cent. $\text{CH}_4$ )	Acetylene-Air (9.5 per cent. $\text{C}_2\text{H}_2$ )	
25	67	285	4.2
50	93	315	3.4
90	105	335	3.2

The mixture at the lower limit of inflammability, horizontal propagation of flame, contains 2.7 per cent. of acetylene. The upper limit is indeterminate, exothermic decomposition of excess,

of acetylene, with deposition of carbon, taking place after a percentage of acetylene of about 17 is exceeded. The speed at which flame travels in the latter mixtures is slow, but does not decrease much with increased acetylene content, as is shown in Fig. 1. According to Le Chatelier, propagation of flame can be obtained (in a tube 40 mm. in diameter) with mixtures containing up to 64 per cent. of acetylene, the speed at the limit being about 5 cm. per second.

Figs. 2—6 reproduce some characteristic appearances of the flames. Each tube was partly covered with black paper, leaving a horizontal slit 5 mm. broad and 30 cm. long, which was focussed on the revolving film. A strip of paper 1 cm. broad divided the slit into two portions, each 14.5 cm. long; this strip appears as a black central line on the photographs. The slit began 10 cm. from the open end, where ignition was effected.

In each instance the flame should be pictured as travelling horizontally from left to right over a measured distance, while the film is moving vertically at a known speed. A curve is thus traced, each point on which has for abscissa the distance travelled by the flame and for ordinate the time that has elapsed since its first appearance at the slit.

*Fig. 2.  $C_2H_2$ , 5.40 per cent.*—A mixture of the same composition inflamed in tubes of 12.5, 25, and 50 mm. internal diameter and photographed on the same film, the peripheral speed of the drum to which it was attached being 57.6 cm. per second in each instance. The increase of speed of flame with increased diameter of tube is well illustrated by this photograph, and is at once apparent from the angles of inclination of the images. The speeds are: 12.5 mm. tube (*A*), 120 cm. per sec.; 25 mm. tube (*B*), 140 cm. per sec.; 50 mm. tube (*C*), 160 cm. per sec.

*Fig. 3.  $C_2H_2$ , 15.00 per cent.*—A mixture of the same composition inflamed in tubes of 12.5, 25, and 50 mm. internal diameter. The speed of the film in each instance was 96 cm. per second. It will be seen that with each of the tubes of larger diameter the uniform movement gave place to the vibratory movement after the flame had traversed half the length of the slit, a distance of about 25 cm. from the open end of the tube. The increase in the mean speed of the flame when this transition takes place is well marked.\* Only the left-hand halves of the curves

\* It is necessary here to note that a distinction must be drawn between the vibrations of large amplitude, accompanied by enhanced mean speed of flame, and the undulations, which are without effect on the speed of the flame, apparent during the "uniform movement" in the larger tubes. The cause of these undulations is explained later.

FIG. 2

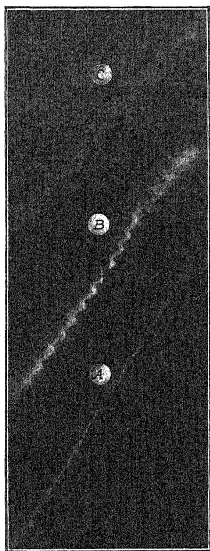
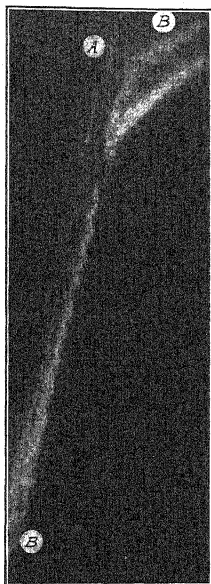


FIG. 3.



[To face page 582.]





can be used for calculating the speeds of the uniform movement, which are: 12.5 mm. tube (*A*), 70 cm. per sec.; 25 mm. tube (*B*), 78 cm. per sec.; 50 mm. tube (unlettered), 85 cm. per sec.

*Fig. 4.*—Flame travelling in a tube 90 mm. in diameter, the mixture containing 9.45 per cent. of acetylene. Speed of film, 96 cm. per sec. The speed of the uniform movement of this flame (335 cm. per sec.) is the fastest recorded for any mixture of acetylene and air during the course of this research.

*Fig. 5.*—Flame travelling in a mixture containing 15.55 per cent. of acetylene photographed in a tube of 25 mm. internal diameter. Speed of film, 96 cm. per sec. This mixture contains a considerable excess of acetylene above that required for complete combustion of the oxygen. Secondary combustion took place, air being drawn in from the open end of the tube, whilst the initial flame was travelling a distance of 27—28 cm.; the vibratory movement, with enhanced mean speed of the flame, was then developed.

A feature, common to all the photographs of the flames in the tubes of larger diameter, is the undulating character of the flame front during the uniform movement. The undulations are due to resonance induced in the tubes at the moment of ignition, in part by the compression wave or pulse produced when the suddenly ignited gases expand, and in part by the pulse or train of pulses arising from the source of ignition itself. This, in the majority of the experiments, was a series of secondary discharges across a 3 mm. gap 3 cm. from the open end of each tube, obtained from a "6-inch" induction coil with a current of 10 amperes in the primary circuit. A single such discharge produces a pulse of considerable intensity (see, for example, Töpler, *Ann. Phys. Chem.*, 1867, [ii], 131, 33; 1868, 134, 194), and it is clear from Fig. 6 that the series of discharges used to cause ignition of the mixtures was largely operative in producing the more pronounced undulations of the flame during the uniform movement.

For this photograph (*Fig. 6*), a mixture containing 5.4 per cent. of acetylene was ignited in a tube 25 mm. in diameter (*A*) by means of a small hydrogen flame held at the mouth of the tube, and (*B*) by the secondary discharge at the spark-gap 3 cm. within. Both photographs were taken on the same film (speed 55 cm. per second), and the images were good enough to fall close together, so that comparison between them is facilitated. It will be seen that *A* exhibits but slight signs of an undulatory motion of the flame during the uniform movement, whilst in *B* the undulations are well defined and similar in general character to those appearing in the majority of the photographs. The mean speed of the

flame (141 cm. per second) is not affected by the undulations.

No rigid uniformity in the manner of ignition of the mixtures was attempted when determining the speeds recorded in Fig. 1; for, provided that the flame is allowed to travel a sufficient distance before measurement of the speed of the uniform movement is made, the initial impetus given to the flame by the spark dies away. A tapping key was employed, the trembler of the induction coil being allowed to function in the usual manner, and no doubt the discharge was maintained during a longer period in some instances than in others. Experiment showed that prolonged passage of the discharge after ignition had been effected sometimes resulted in the appearance in the photographs of the flames of small undulations superposed on the main undulations, but did not otherwise affect their character.

There remain to be considered the faint undulations apparent in Fig. 6, *A*. These are evidently due to resonance set up in the column of gases in the tubes by the slight shock imparted to it at the moment of ignition, for if great care be taken to avoid any disturbance at the mouth of the tube when igniting the gases, no undulations of the flame appear. In Fig. 7 are reproduced the photographs of flames travelling in a mixture containing 5.15 per cent. of acetylene. For (*A*) ignition was by a small jet of burning hydrogen introduced through a hole 4 cm. from the open end of the tube, whilst for (*B*) a large, flat flame of hydrogen, which more than covered the cross-section of the tube, was used, and this was held momentarily across the mouth of the tube in such a manner that ignition of the mixture took place there simultaneously over the whole surface. With the small source of ignition at a point 4 cm. within the tube, an undulatory motion is imparted to the flame of a more pronounced character than when a similar small source of ignition is held at the mouth of the tube (Fig. 6, *A*). With the large source of ignition (*B*), the propagation of flame is initially absolutely uniform. The speed of the film for these photographs was 96 cm. per second.

Fig. 8 shows the effect of varying the intensity of the compression wave or pulse produced on ignition by varying the volume of mixture contained between the point of ignition and the open end of the tube. The photographs record the progress of the flame from the point of ignition, which was 1 cm. within the tube for (*A*), 4.5 cm. within for (*B*), and 12 cm. within for (*C*). A mixture containing 5.8 per cent. of acetylene was used, and the tube was 25 mm. in diameter. The speed of the film was 100 cm. per

second. Ignition was by a single discharge across a 3 mm. gap produced by breaking a current of 6.6 amperes in the primary of a "10-inch" X-ray coil, the trembler of which was locked.

The "uniform movement" of the flame lies towards the right-hand side of each photograph, that direction of travel being towards the closed end of the tube. Towards the open end the flames travel rapidly, and some of the mixture is projected into the air and burns there. It is clear that the larger the volume of the mixture thus rapidly ignited, and the more intense in consequence the compression wave produced, the greater is the amplitude of the undulations produced in the uniform movement of the flame. When the point of ignition is 12 cm. within the tube, the motion of the flame cannot be regarded as "uniform" at all. (In this connexion, see T., 1917, 111, 1055.)

It may be remarked that the undulatory motion of the flames, even when accentuated by the use of a powerful secondary discharge to ignite the mixtures, is not apparent from direct observation. Its occurrence is rendered evident, however, not only by photographic means, but sometimes also by the appearance along the glass tubes of rings of moisture deposited at regular intervals after the flames have passed. Neyreneuf (*Compt. rend.*, 1880, 91, 321) appears to have obtained similar effects in short tubes coated on the inside with paraffin wax.

The proof that these undulations are indeed resonance effects lies in the close correspondence between their frequencies as determined from the photographs and as calculated from the dimensions of the tubes. Each tube being closed at one end and open at the other, the mode of vibration of the column of gases to give the fundamental tone results, according to Bernoulli's theorem, in an approximate frequency  $n = u/4l$ ,  $u$  being the velocity of sound in the gases and  $l$  the length of the tube. This approximation assumes a loop, with no pressure variation, at the open end of the tube, a condition which does not obtain. An "end correction" must be applied, which with flanged pipes amounts to about  $0.82 r$ , and with unflanged pipes to about  $0.60 r$  (see Rayleigh, "The Theory of Sound," Vol. 2, p. 183. London, 1896). That is to say, the length of the tube must be increased by  $0.82 r$  if flanged and by  $0.60 r$  if unflanged before Bernoulli's theorem is applied.

Of the tubes used in the experiments, that of 50 mm. diameter alone was flanged. The observed frequencies of the undulations during the uniform movement of the flames, the dimensions of the tubes, and the calculated frequencies for the fundamental tone

during the longitudinal vibration of air in cylindrical pipes of those dimensions, are given in the table that follows:

Frequency of undulations during uniform movement of flame.	Dimensions of tube		Calculated frequency of fundamental tone of tube.
	Length.	Diameter.	
63	130 cm.	1.25 cm.	63.5
59	141	2.5	58.4
65	126	5.0 (flanged)	64.8
58	140	9.0	58.1

The value taken for the velocity of sound when calculating the frequencies of the fundamental tones of the tubes was 332 m. per second, the velocity in open air at 15°. The velocity in the mixtures in the tubes would vary slightly with the composition of the mixture and the diameter of the tube, but not to a sufficient extent to affect seriously the calculated frequency.

#### EXPERIMENTAL.

The only part of the experimental arrangements requiring further description is the camera. This consisted of a light-tight box furnished with a lens of quartz 13 cm. in diameter, and containing a drum for the reception of the film, which could be revolved at a high speed.

The focal length of the lens was 17 cm., and its position was fixed once and for all in relation to (1) the tube to be photographed, and (2) the film, so that the size of the image obtained was nearly one-quarter that of the object, the distance of the film from the lens being 20.5 cm.

The drum was 47 cm. in circumference and 10 cm. wide. Its spindle projected at either end through the sides of the camera, and carried at the one end a pulley to receive the drive of an electric motor and at the other end a reduction gearing. This gearing communicated with another drum, of the same diameter as that within the camera, used to receive, on a smoked paper chart, the record of a tuning-fork. The speeds of revolution of the two drums were as 1:32.

All the records of speeds obtained by the photographic method are given in the table that follows. As a check on the method, a series of determinations was made in the 12 mm. tube, using the "screen-wire" method as employed by Haward and Sastry; these determinations are placed within brackets in the table.

		Speed of uniform movement of flame.			
Diameter of tube in mm. = Acetylene in air. Per cent.		12.5	25	50	90
2.75	—	—	—	—	40
3.30	(26)	—	—	—	—
3.45	25	41	60	—	—
3.55	—	—	—	—	69
4.00	(55)	—	—	—	—
4.40	—	—	—	—	115
4.60	82	95	115	—	—
5.30	(120)	—	—	—	—
5.40	120	140	160	—	—
5.80	—	—	—	—	195
6.00	(155)	—	—	—	—
6.10	158	172	205	—	—
7.00	—	—	—	—	265
7.05	205	225	250	—	—
7.15	(205)	—	—	—	—
7.40	220	240	270	—	—
7.95	—	—	—	—	310
8.00	(252)	—	—	—	—
8.15	258	270	303	—	—
8.60	(260)	—	—	—	—
8.90	265	282	312	—	—
9.00	(268)	—	—	—	—
9.45	(265)	—	—	—	335
9.90	266	280	310	—	—
10.35	260 (265)	278	304	—	—
10.55	—	—	—	—	320
10.65	(255)	—	—	—	—
11.00	(235)	—	—	—	—
11.60	206 (210)	245	283	—	—
11.85	—	—	—	—	285
12.30	—	—	—	—	260
12.40	(160)	—	—	—	—
12.50	150	191	230	—	—
13.25	115	145	175	—	220
13.30	(115)	—	—	—	—
14.00	90	100	115	—	—
15.10	70	78	85	—	—
15.30	—	—	—	—	84
15.60	(65)	—	—	—	—
16.00	60	68	72	—	—
18.20	—	—	60	70	—

The acetylene was obtained compressed in cylinders, without acetone as solvent, and was of a high degree of purity. The air mixtures were made in metal gas-holders over brine, and were analysed before use.

ESKMEALS,  
CUMBERLAND.

[Received, May 8th, 1919.]

XLVIII.—*The Preparation of Diacetoneamine.*

By ARTHUR ERNEST EVEREST.

THE methods for the preparation of diacetoneamine which are described in the literature are laborious and by no means satisfactory, and this applies whether the preparation is through mesityl oxide or by the direct action of ammonia on acetone.

Having need of considerable quantities of the compound, as the starting point for synthetic work, the author tried to find a method which would be both simple in action and satisfactory in respect of yield. The process described below, which was the result of the work, is successful in both respects, and furthermore eliminates almost completely the laborious recovery of mixtures of alcohol and acetone which are formed in the usual process of preparation from acetone and ammonia (see the table below). It enables considerable quantities of diacetoneamine to be prepared with ease and comparative rapidity, and thereby makes this product much more available as a starting point for synthetic work.

One of the chief difficulties in the production of diacetoneamine from acetone and ammonia is the comparatively small amount of ammonia which acetone will dissolve, a fact that necessitates several slow re-saturations being resorted to at intervals of five to seven days. Even when this course is adopted, a large proportion of the acetone remains unchanged. The author has made use of anhydrous calcium chloride to obviate this difficulty. By this means, the whole of the ammonia required can be passed into the reaction mixture in quite a short time, and, moreover, not only does the calcium chloride store up the requisite ammonia, but the water formed as the reaction proceeds is taken up by it, whereby a concentrated solution is formed which separates as a distinct layer and can be removed when the reaction is completed.

## EXPERIMENTAL.

Acetone (1160 grams) and anhydrous calcium chloride (200 grams) were introduced into a vessel fitted with a reflux condenser (to prevent loss of acetone during the introduction of ammonia) and an inlet for ammonia. The vessel was then placed in cold water and ammonia (from a cylinder) blown into the mixture as rapidly as the liquid would absorb it (100 grams of ammonia were introduced in quite a short time without any appreciable loss).

Much heat was developed during the addition of the ammonia, but with an effective condenser no loss resulted from this. The introduction of ammonia was continued until the amount absorbed was equal to the weight of the calcium chloride used (200 grams). If it was found that the liquid became nearly saturated before the requisite amount of ammonia had been added (this was rarely the case), the addition of ammonia was stopped, the vessel allowed to remain some eight to ten hours (say overnight), and a further amount of ammonia then added. Before the whole of the ammonia had been introduced, water had usually commenced to separate, a fact that had no detrimental effect on the result.

When 200 grams of ammonia had been blown in, the vessel was allowed to remain at the ordinary temperature for eight to nine days. It was found to be advantageous to shake well once a day during this period. As the reaction proceeded, the compound of calcium chloride and ammonia decomposed, and the products dissolved in the water formed by the reaction, the calcium chloride solution thus produced forming the lower layer in the vessel. Towards the end of the reaction, the upper layer became quite viscous and developed a pale yellow colour, whilst the odour of the amine became noticeable alongside that of ammonia.

When the reaction was completed, the layers were separated, care being taken that all the calcium chloride was removed, as when this was not done, considerable trouble was caused in the filtrations later by the calcium oxalate formed in working up the product. The aqueous layer when extracted with ether yielded a small additional quantity of amine, but in general it was not considered profitable to carry out this operation, and the yields stated below do not include such extractions.

After separation, the amine layer (top) was placed in a vessel and dry air drawn rapidly through it for several hours, whereby a large proportion of the excess of ammonia was removed. The liquid thus obtained possessed a strong odour of the amine. The amount of oxalic acid required for the formation of the hydrogen oxalate was determined (by titration with standard oxalic acid), this was dissolved in alcohol, three times the volume of the reaction mixture being used, and the amine then poured slowly into the alcoholic solution, the whole being kept well agitated. Rectified spirit (B.P.) gave with this process as good results as absolute alcohol had given with other processes, this being due to the fact that the water produced in the reaction was removed, whilst in the older methods it remained in the reaction mixture.

When all the amine had been added, the product, without filtration, was placed in a distilling flask and distilled up to 75°, during

which process a small amount of a mixture of acetone and alcohol passed over (from 1160 grams of acetone, only about 45 grams remained unacted on and passed over in this mixture). At 75°, the distillation was discontinued, and the contents of the distilling flask were rapidly filtered hot. The filtrate, on cooling, deposited diacetoneamine hydrogen oxalate in crystalline condition, which was collected, washed with alcohol, and dried. The solid residue from the hot filtration yielded a small additional quantity of the product when extracted with fresh hot alcohol. From the total mother liquors, a considerable further quantity of pure product was obtained by distilling them on a water-bath until nothing further passed over, allowing the residue to remain for about twenty-four hours in the cold, collecting the crystals which separated, and washing them with alcohol. A certain amount of syrup remained as a by-product, and in this a small amount of triacetoneamine was detected.

By the above method, 800 grams of diacetoneamine hydrogen oxalate (m. p. 125—127°), containing about 1 per cent. of ammonium hydrogen oxalate (see note at end of paper), could be regularly obtained. Of this yield, about 600 grams were obtained from the first deposition and about 200 grams from the liquors and by extraction of the solid residues.

The following table gives comparative results as obtained with the method described above (*a*), and by the direct action of ammonia on acetone without the use of calcium chloride (*b*).

	( <i>a</i> )	( <i>b</i> )
Acetone taken .....	1045 grams	2100 grams
„ recovered .....	45 „	1100 „
„ used .....	1000 „	1000 „
Acetone-alcohol mixture fractionated to recover acetone and alcohol ...	100 c.c.	2250 c.c.
Alcohol used .....	3 litres (rectified spirit, B.P.)	2½ litres (absolute).
„ recovered .....	All; somewhat diluted.	All; considerably diluted.
Oxalic acid used .....	1050 grams.	1060 grams.
Time of keeping .....	8½—10 days.	24—28 days.
Number of saturations with ammonia .....	One.	4, at intervals of 5—7 days.
Ammonia used (anhydrous)	190 grams.	210 grams.
Yield .....	724 „	434 „
By-product: ammonium hydrogen oxalate .....	340 „	440 „

The work described above was carried out in the chemical laboratories of University College, Reading, in February, 1916, and the author desires to thank the Sectional Chemical Committee



of the Royal Society, at whose request the preparation of the diacetoneamine was undertaken, for permission to publish the results.

#### APPENDIX.

##### *Note on Diacetoneamine Hydrogen Oxalate and Vinylacetoneamine Oxalate.*

By ARTHUR ERNEST EVEREST and HAROLD ROGERSON.

In connexion with the work on the new process for the preparation of diacetoneamine described above, it was desirable that a ready means of checking the purity of samples of diacetoneamine hydrogen oxalate and of vinylacetoneamine oxalate should be available. It was further necessary to prove the identity of the products obtained.

In view of the fact that no melting points have been recorded in the literature for these substances, previous workers have at times resorted to the expedient of converting either of the above compounds into a salt of vinylacetonealkamine, liberating the free base, and determining the melting point of this. The fact that this method is obviously unsatisfactory, and that time did not permit of ultimate analysis, led one of us (A. E. E.) to test pure specimens of the above compounds for melting point. It was found that both could be identified by this means. At the same time, the other (H. R.), who was also preparing quantities of these compounds, had quite independently observed that they had sharp melting points. The determinations were therefore mutually confirmed by exchange of specimens.

#### EXPERIMENTAL.

##### (a) *Diacetoneamine Hydrogen Oxalate.*

A pure specimen of diacetoneamine hydrogen oxalate melts fairly sharply at 126—127° to a clear, colourless liquid which, on cooling, sets to a mass of crystals, which again melt at 126—127°. The presence of ammonium hydrogen oxalate in the product causes opalescence in the liquid that results on melting, but has little effect on the melting point. Thus:

Pure diacetoneamine hydrogen oxalate melts to a clear liquid at 126—127°.

Pure diacetoneamine hydrogen oxalate + 1 per cent. of ammonium hydrogen oxalate melts at 125.5—127°.

Pure diacetoneamine hydrogen oxalate + 5 per cent. of ammonium hydrogen oxalate softens then melts at  $124.5-126^{\circ}$ .

Pure diacetoneamine hydrogen oxalate + 10 per cent. of ammonium hydrogen oxalate softens more noticeably then melts at  $124-125.5^{\circ}$ .

If much ammonium hydrogen oxalate is present in the sample, no melting point is observed, only a softening taking place. This may account for the fact that no melting point has been recorded previously.

A rough approximation of the amount of ammonium hydrogen oxalate in a sample of diacetoneamine hydrogen oxalate may be obtained by observation of the degree of opalescence shown when it melts, but for more accurate determinations an extraction of the diacetoneamine salt from the sample by boiling absolute alcohol and weighing of the residue is recommended.

#### (b) *Vinyldiacetoneamine Oxalate.*

When this compound is prepared from diacetoneamine hydrogen oxalate which contains ammonium hydrogen oxalate, the latter passes through into the product. The presence of ammonium hydrogen oxalate has the same effect on the melting point of vinyldiacetoneamine oxalate as it has on that of the diacetoneamine salt. If sufficient of the ammonium salt is present, no melting point can be observed, mere shrinkage and change of colour taking place.

Pure vinyldiacetoneamine oxalate, prepared from pure diacetoneamine hydrogen oxalate and freed from the latter and from oxalic acid by twice boiling with a fairly large quantity of absolute alcohol, filtering hot, and finally washing with boiling absolute alcohol and drying in a vacuum over concentrated sulphuric acid, melts sharply at  $184-185^{\circ}$  with the evolution of gas and development of a yellow colour. The presence of diacetoneamine hydrogen oxalate in the vinyl compound affects the melting point of the latter considerably and makes it less sharp.

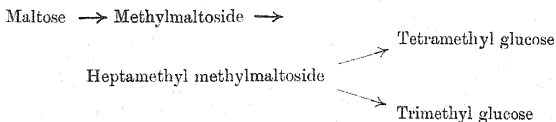
These observations were made at University College, Reading, and at Guy's Hospital Medical School, in February, 1916.

[Received, April 16th, 1919.]

# XLIX.—*The Constitution of Maltose. A New Example of Degradation in the Sugar Group.*

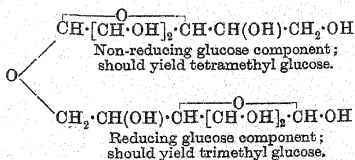
By JAMES COLQUHOUN IRVINE and JAMES SCOTT DICK.

IN the following paper are described the principal results obtained in an investigation undertaken some years ago with the object of determining the constitution of maltose. The standard process was adopted of complete methylation of the disaccharide, followed by identification of the two alkylated sugars produced on hydrolysis, and the series of reactions as originally planned may be represented by the following synopsis:

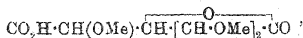


Although the above scheme has not been fully realised, it has been possible to confirm and supplement the earlier results of Purdie and Irvine (T., 1905, 87, 1022), who showed that the non-reducing glucose component of maltose possesses the butylene-oxide structure, and thus yields crystalline tetramethyl glucose as one product of the above reactions.

This result establishes the constitution of one half of the disaccharide molecule, but, owing to an unexpected degradation of maltose encountered in the course of the work, we have been unable to isolate the trimethyl glucose which should be formed as a second hydrolysis product from a fully methylated maltoside. On the basis of the accepted constitution of maltose, the operation of the series of reactions should give, in addition to tetramethyl glucose, the butylene-oxide form of trimethyl glucose described by Purdie and Bridgett (T., 1903, 83, 1037). This is shown below:



The identification of the particular form of trimethyl glucose to be expected is, however, difficult in view of the failure of this sugar to give crystalline derivatives, and accordingly, as a necessary preliminary to the present research, we re-examined the compound and determined its physical constants as standards of comparison. In addition, the constitution provisionally assigned to the sugar has been confirmed by a study of its decomposition products. When oxidised drastically by means of nitric acid, the essential product proved to be the monolactone of trimethylsaccharic acid,



a result which confirms the view that the primary alcohol group in the parent sugar is unsubstituted.

The data thus accumulated proved, however, of little service in the present research, which developed an unexpected but interesting complexity. In preparing the necessary methylmaltoside, we adopted the method described by Mills (*Chem. News*, 1912, 106, 165), in which hepta-acetyliodomaltose is converted into the corresponding acetylated methylmaltoside and the acyl groups are removed by hydrolysis. In the light of subsequent events, this proved to be an unfortunate decision. The various reactions appeared to proceed normally, but, on applying the silver oxide process to the " $\beta$ -methylmaltoside," we obtained, after three methylations followed by vacuum distillation, a colourless syrup which gave on analysis by Zeisel's method figures agreeing closely with those required for a *hexamethyl methylmaltoside*. In the belief that the methylation was incomplete, further treatments with the alkylating mixture were carried out, but this had no effect on the composition. As a second preparation gave precisely the same result, although the silver oxide reaction was repeated five times, and this was followed by two further methylations, one by means of methyl sulphate and the other by diazomethane, we were forced reluctantly to the conclusion that steric hindrance had interfered completely with the methylation of one hydroxyl group of the maltose molecule.

The results of combustions were indecisive, and the correct interpretation was forthcoming only when the supposed hexamethyl methylmaltoside was hydrolysed, and the two sugars thus produced were separated by distillation in the high vacuum of the Gaede pump. As already mentioned, crystalline tetramethyl glucose was readily obtained as the fraction of lower boiling point, but the remaining product distilled only with the greatest difficulty under

a pressure of 0.1 mm., and could not be induced to crystallise. Examination showed this viscous syrup to be a reducing sugar and to possess the composition of a *dimethyl pentose*, so that clear evidence was thus obtained that, at some stage of the successive reactions, degradation of the maltose molecule had taken place to give derivatives of a sugar containing eleven carbon atoms in the chain. Owing to the close coincidence in the calculated compositions of a highly methylated methylmaltoside and a hexamethyl methylglucopentoside, it was impossible to detect this degradation before hydrolysis, and, owing to the unexpected nature of the result, it was necessary to obtain confirmatory evidence. The dimethyl pentose was therefore converted successively into the corresponding dimethyl methylpentoside and trimethyl methylpentoside, and each compound gave on analysis figures which agree closely with the above explanation. Further, the values found for the specific rotations of these compounds agree with the idea that they are derivatives of arabinose, and the corresponding nomenclature is accordingly employed in the experimental part.

There is little doubt that the degradation took place during the decomposition of maltose octa-acetate by means of hydrogen iodide, and is due to a species of reduction which is unusual in the sugar group. No doubt such a reaction, when once commenced, would be progressive, but in the twelve experiments conducted by us, the change was approximately arrested at a stage when the main product consisted of a derivative of a  $C_{11}$  sugar. The maltose originally used was of high purity, and the octa-acetate prepared from it also conformed to accepted standards. On the other hand, the supposed "hepta-acetyl methylmaltoside," obtained after reaction with hydrogen iodide followed by treatment with methyl alcohol, was abnormal. Although apparently a definite chemical individual, we were unable by any process of crystallisation to raise the melting point above  $115-117^{\circ}$ , whereas the recorded values are higher (Fischer and Armstrong,  $121-122^{\circ}$ ,  $125-126^{\circ}$ ; Königs and Knorr,  $128-129^{\circ}$ ). Fischer has, however, remarked on the difficulty in obtaining this compound pure, and as the method of preparation adopted by us might lead to the production of non-separable  $\alpha$ - and  $\beta$ -forms showing a lower melting point, there was no reason at the time to doubt the nature of the compound.

The interruption of our collaboration, due to the War, has prevented us from studying the degradation of sugars by means of hydrogen iodide on more general lines, but the subject is evidently important, as the possibility is opened out of degrading maltose in an acid system and comparing the results with those already

obtained by regulated oxidation in alkaline solution (Lewis and Buckborough, *J. Amer. Chem. Soc.*, 1914, **36**, 2385).

Meanwhile, in a separate research, the results of which will be communicated at an early date, the complete structure of maltose has been established by a method free from the complications now described.

#### EXPERIMENTAL.

##### *Preparation of Maltose Octa-acetate.*

As the preparation of this compound in a pure condition presents considerable difficulty, an account may be given of the method which in our experience proved the most satisfactory.

Pure maltose was acetylated by means of acetic anhydride and sodium acetate in the manner described by Herzfeld (*Annalen*, 1883, **220**, 200), but the reaction was continued for thirty minutes, after which the hot syrup was poured into cold water. On stirring vigorously, the product solidified, and the disintegrated solid was collected, dissolved in alcohol, and the solution neutralised with barium carbonate. The filtered solution was then poured into water, and the solid acetate which separated was collected on a filter and thereafter dried in a vacuum. On extracting the dry crystals repeatedly with a large excess of boiling ether, the impurities remained undissolved, and on removal of the solvents from the united extracts, the acetate was obtained in good yield. One recrystallisation from hot alcohol was then sufficient to give the pure compound melting at 157°.

##### *Action of Hydrogen Iodide on Maltose Octa-acetate.*

Sixty grams of the acetate, in portions of 5 grams, were treated in methylene chloride solution with carefully purified hydrogen iodide, as described by Mills (*loc. cit.*). The excess of the gas and the solvent were removed in a high vacuum, and the residual syrup was at once dissolved in dry methyl alcohol, and the solution shaken with silver carbonate until free from iodine. On concentration of the filtrate, the product crystallised readily, but even after repeated crystallisation the melting point could not be raised above 117°.

The yields obtained in the twelve preparations varied considerably, and were in no case more than 60 per cent. of the theoretical amount. Apparently an important factor is to minimise the time during which the acetate is in contact with hydrogen iodide to less than thirty minutes, and to remove the excess of the gas as rapidly

as possible. Otherwise the amount of syrup formed is increased and the proportion of crystalline product seriously diminished.

The removal of the acetyl groups from the supposed hepta-acetyl methylmaltoside was effected in the usual way by shaking with aqueous barium hydroxide, the ultimate product being a glucosidic syrup, which proved to be methylglucoarabinoside. Throughout all the above reactions, the customary precautions were taken to prevent molecular rupture, and the operations were thus extremely tedious.

*Methylation of Methylglucoarabinoside.*

No details of this reaction need be given, as it was conducted precisely as described in earlier papers dealing with the methylation of glucosides by means of silver oxide and methyl iodide. After two alkylations in methyl-alcoholic solution, the product was freely soluble in methyl iodide, and consequently no extraneous solvent was required in the final methylations. The product, which was a clear, viscid syrup, was purified by fractionation in a high vacuum, and the following table shows that successive treatments did not increase the methoxyl content above a fixed maximum.

Number of methylations.	B. p.	$n_D$	Methoxyl.
4	188—190°/0.35 mm.	1.4692	50.34 per cent.
5	195°/0.1 mm.	1.4688	50.66
5	205—208°/0.4 mm.	1.4695	52.2, 50.79 per cent.
6	200—203°/0.4 mm.	1.4689	50.45

In a second preparation, otherwise duplicate, the treatment was extended by one methylation by means of methyl sulphate and sodium hydroxide, and finally by diazomethane in ethereal solution, but without alteration in the analytical figures or physical constants of the product. The mean of several consistent analyses gave:

C=52.11; H=8.21; OMe=50.9 per cent.

Heptamethyl methylmaltoside:

$C_{20}H_{32}O_{11}$  requires C=52.86; H=8.37; OMe=54.63 per cent.

Hexamethyl methylmaltoside:

$C_{19}H_{30}O_{11}$  requires C=51.81; H=8.18; OMe=49.3 per cent.

Hexamethyl methylglucoarabinoside:

$C_{18}H_{28}O_{10}$  requires C=52.68; H=8.29; OMe=52.9 per cent.

The results fail to discriminate between the alternatives, and the molecular weight, determined in benzene solution by the cryoscopic method, was equally inconclusive.

Found: 425.

$C_{19}H_{36}O_{11}$  requires 440;  $C_{18}H_{34}O_{10}$  requires 410.

On the evidence yielded by hydrolysis, the compound was finally shown to be essentially hexamethyl methylglucoarabinoside ( $C_{18}H_{34}O_{10}$ ).

The new glucoside is a viscid, colourless syrup freely soluble in organic solvents generally, but less so in water. Presumably the specimen examined would consist of both  $\alpha$ - and  $\beta$ -forms, so that the specific rotations have only a qualitative significance, but, as is usually the case with methylated compounds possessing the glucose configuration, the activity was but little affected by the nature of the solvent.

Solvent.	c.	$[\alpha]_D^{20}$ .
Water .....	4.875	+78.8°
Methyl alcohol .....	5.609	77.5
Ethyl alcohol.....	5.316	75.9
Acetone .....	5.103	76.9

#### *Hydrolysis of Hexamethyl Methylglucoarabinoside.*

Preliminary experiments showed that the double hydrolytic change of removing the glucosidic methyl group and liberating the two constituent aldoses was best effected by boiling a 5 per cent. solution of the above compound in 5 per cent. aqueous hydrochloric acid. This method was accordingly applied to 38 grams of the glucoside, boiling under reflux being continued until the rotation diminished to a constant value, which it did in thirty minutes. The acid was neutralised with barium carbonate, the filtered solution evaporated to dryness under diminished pressure, and the residue extracted with boiling alcohol. After removal of the alcohol, the residual syrup was dissolved in hot acetone, the solution being again filtered and evaporated. The mixed sugars produced in the hydrolysis were obtained in this way as a pale yellow syrup, and were separated by fractionation at the Gaede pump.

A definite first fraction, amounting to 40 per cent. of the total weight, was collected at  $125^{\circ}/0.5$  mm. as a moderately mobile liquid, but the remainder of the material distilled only with the greatest difficulty, and presented the appearance of a glass. As much decomposition took place in the later stages of the distillation, no attempt was made, after the first preliminary trial, to distil this product, heating being continued only until the first fraction had been removed.

The more volatile sugar crystallised readily, and, after draining on porous porcelain and two recrystallisations from light petroleum,



was identified as butylene-oxidic tetramethyl glucose melting at 85—87°. (Found: C=50.62; H=8.41; OMe=52.46.  $C_{10}H_{20}O_6$  requires C=50.85; H=8.47; OMe=52.54 per cent.)

Mutarotation in alcohol: Initial  $[\alpha]_D^{20} + 104.9^\circ \rightarrow$  Final 83.9°.

*Identification of Dimethyl Arabinose.*—The less volatile sugar solidified on cooling to a glass, and no crystallising medium could be found for the compound, as it is very readily soluble in water or organic solvents, with the exception of light petroleum. It reduces Fehling's solution readily, and is thus a reducing sugar, but gave only syrupy products when treated with aniline, hydroxylamine, or with phenylhydrazine and acetic acid. In approximately 5 per cent. solution, the compound was dextrorotatory:

Solvent.	$[\alpha]_D^{20}$ .
Water .....	+57.7°
Ethyl alcohol.....	50.6
Acetone .....	56.9

Before determining the activity or the analytical composition, the compound was further purified from traces of tetramethyl glucose by solution in dry ether and the addition of light petroleum, after which the syrupy precipitate was dried in a high vacuum.

The mean of three consistent analyses showed that the sugar was neither the di- nor the tri-methyl glucose expected.

Found: C=47.63; H=7.99; OMe=35.28.

Dimethyl arabinose:

$C_7H_{14}O_5$  requires C=47.19; H=7.86; OMe=34.83 per cent.

Dimethyl glucose:

$C_8H_{16}O_6$  requires C=46.13; H=7.73; OMe=29.8 per cent.

Trimethyl glucose:

$C_9H_{18}O_6$  requires C=48.63; H=8.15; OMe=41.9 per cent.

All the results, and more particularly the methoxyl content, point to the idea that the sugar is a dimethyl arabinose, but further identification was obtained by converting the compound into the corresponding methylpentoside by Fischer's method.

*Dimethyl methylarabioside* proved to be a colourless syrup (b. p. 120°/0.1 mm.,  $n_D$  1.4620) devoid of action on Fehling's solution until hydrolysed.

Found: C=50.38; H=8.60; OMe=48.9.

$C_8H_{16}O_5$  requires C=50.00; H=8.33; OMe=48.5 per cent.

Further confirmation of the composition of the parent sugar was obtained by subjecting the above pentoside to the silver oxide reaction, so as to produce trimethyl methylarabioside, which was

isolated as a colourless, mobile liquid (b. p. 94—96°/0.08 mm.,  $n_D^{20}$  1.4460).

Found: C=52.18; H=8.80; OMe=60.1, 60.8.

$C_9H_{15}O_5$  requires C=52.42; H=8.73; OMe=60.2 per cent.

The whole series of analytical results thus consistently supports the view that all the compounds examined are derivatives of a pentose, and not of a hexose. Considering their method of formation, they would consist of mixtures of  $\alpha$ - and  $\beta$ -forms, and consequently specific rotations need not be quoted, but the fact that in each case the compounds are strongly dextrorotatory justifies the opinion that they are derived from arabinose, and this is embodied in the nomenclature used.

*Trimethyl  $\alpha$ -Methylglucoside and Trimethyl Glucose.*

The above compounds are already known, but were re-examined for reasons stated in the introduction. Both substances are viscid syrups and yield no crystalline derivatives, so that their identification rests chiefly on the determination of their specific rotations. Unfortunately, the values found by different observers show considerable variation, a fact which may be explained by the difficulty encountered in fractionating syrups of high boiling point under the vacua given by an ordinary water pump, and accordingly we conducted our final distillations under the highly diminished pressure of the Gaede pump.

Fifty grams of  $\alpha$ -methylglucoside were dissolved in methyl alcohol and methylated by means of silver oxide (150 grams) and methyl iodide (183 grams), exactly as described by Purdie and Bridgett (*loc. cit.*). After two alkylations, the product was isolated in the usual way and subjected to systematic fractionation, as a result of which 29.5 grams of pure material were obtained after six distillations. The syrup boiled at 160—161°/10 mm., showed  $n_D^{20}$  1.4606, and gave  $[\alpha]_D^{20} + 134.6^\circ$  in absolute alcohol, a value which is not far removed from the specific rotation quoted by Purdie and Irvine (T., 1903, 83, 1021).

On hydrolysis with aqueous hydrochloric acid, the glucoside was converted into trimethyl glucose, the sugar being isolated in the customary manner, and purified by repeated distillations which were continued after satisfactory analytical figures were obtained. The final boiling point recorded was 152—155°/0.02 mm., but the refractive indices and specific rotations shown by the product of different preparations fluctuated widely, although the parent glucoside employed was apparently identical. The

extent of this variation is shown in the two extreme cases quoted below.

In the first preparation, the trimethyl methylglucoside used showed  $n_D$  1.4606 and  $[\alpha]_D^{20} + 134.6^\circ$  in methyl alcohol, whilst in the second the corresponding values were 1.4596 and  $132.4$ . The trimethyl glucose obtained from these two sources showed:

	Preparation I.	Preparation II.
$n_D$ .....	1.4780	1.4768
$[\alpha]_D^{20}$ in water .....	$+48.6^\circ$	$+60.7^\circ$
$[\alpha]_D$ in methyl alcohol .....	48.3	65.3
$[\alpha]_D$ in acetone .....	46.2	58.8

In view of these results, there can be little doubt that the sugar and the glucoside from which it was prepared were mixtures of isomerides, and the identification of  $\beta$ - $\gamma$ -trimethyl glucose must in the meantime depend on oxidation processes.

#### *Oxidation of Trimethyl Glucose.*

3.5 Grams of the sugar were dissolved in 50 c.c. of nitric acid (D 1.7), and the solution was heated to  $80^\circ$  in order to start the oxidation. Thereafter, the mixture was kept at  $65^\circ$  for three hours, then diluted with water, and evaporated to a syrup under diminished pressure. The process of dilution with water and subsequent evaporation was repeated four times, and was followed by three similar treatments, in which alcohol was used as the diluent. As the syrupy product darkened rapidly at  $120^\circ$ , no attempt was made to distil the compound, which was prepared for analysis by heating at  $60^\circ/0.3$  mm. until constant in weight. Analysis showed the substance to be the monolactone of trimethylsaccharic acid.

Found: C=46.07; H=6.33; OMe=37.2.

$C_9H_{14}O_7$  requires C=46.13; H=6.02; OMe=39.7 per cent.

When dissolved in alcohol and rapidly titrated with  $N/10$ -sodium hydroxide, the first neutralisation corresponded with the presence of one carboxyl group, and thereafter the compound behaved as a typical lactone on further titration. The lactonic structure was confirmed by the fact that in absolute alcohol the specific rotation remained practically constant, but diminished to a permanent value when aqueous alcohol was used as solvent.

Solvent.	Initial $[\alpha]_D^{20}$ .		Final $[\alpha]_D$ .
Absolute alcohol .....	$+41.5^\circ$	$\rightarrow$	$+43.0^\circ$ in 48 hours.
50 per cent. alcohol .....	43.2	$\rightarrow$	24.0 .. ..

We desire to express our indebtedness to the Carnegie Trust for a Research Scholarship which enabled one of us to take part in the work, and also to Miss E. S. Steele, who completed the research when our collaboration was interrupted.

CHEMICAL RESEARCH LABORATORY,  
UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,  
UNIVERSITY OF ST. ANDREWS. [Received, May 3rd, 1919.]

### L.—Catalytic Racemisation of Ethyl *l*-Mandelate.

By ALEX. McKENZIE and HENRY WREN.

THE work described in the present communication was suggested by the following observations which have been recorded in the literature dealing with the phenomenon of racemisation.

(1) When an optically active ester is hydrolysed by alkali, it has frequently been found that the product is partly racemised; for example, the specific rotatory power of the barium salt obtained by the action of aqueous barium hydroxide on ethyl *l*-phenylethoxyacetate was only about one-half that of the optically pure salt (McKenzie, T., 1899, 75, 759). Occasionally, the racemisation is even complete; thus, when *l*-mandelic acid was alkylated by a mixture of *n*-propyl iodide and silver oxide, the phenylpropoxyacetic acid isolated from the resulting ester was, contrary to expectation, optically inactive, a result which may now be attributed, in part at least, to the action of the alcoholic alkali employed for the hydrolysis of the ester.\* Another example is afforded by the more recent observation of Rupe and Kerkovius (*Ber.*, 1912, 45, 1398), who obtained optically inactive  $\alpha\beta$ -diphenylpropionic acid as a consequence of the action of alcoholic alkali on *l*-menthyl *l*- $\alpha\beta$ -diphenylpropionate. Moreover, McKenzie and Miss Widdows showed that the acid isolated from the product of the action of a very slight excess of dilute alcoholic potassium hydroxide on ethyl *d*-phenyl-*p*-tolylacetate was quite inactive.

(2) The gradual racemisation of *l*-mandelic acid when heated

\* References on the partial racemisation occurring during the action of alcoholic alkali on optically active esters are the following: McKenzie, T., 1904, 85, 378, 1249; McKenzie and Thompson, T., 1905, 87, 1004, T., 1907, 91, 789; McKenzie and Müller, T., 1907, 91, 1814; McKenzie and Humphries, T., 1909, 95, 1105; McKenzie and Widdows, T., 1915, 107, 702; Wren and Still, T., 1915, 107, 1449; Wren and Williams, T., 1916, 109, 573; Wren, T., 1918, 113, 210.

with alkali was first observed by Holleman (*Rec. trav. chim.*, 1898, 17, 323), whose observations were extended by McKenzie (T., 1904, 85, 385) and by McKenzie and Thompson (T., 1905, 87, 1020). The contrast between the action of aqueous- and ethyl-alcoholic alkali on an optically active acid was studied by McKenzie and Bate (T., 1915, 107, 1681) in the case of *l*-phenylanilinoacetic acid; the effect of the ethyl-alcoholic sodium hydroxide as compared with that of the aqueous alkali was very pronounced, the recovered acids having the values  $[\alpha]_D -4^\circ$  and  $-109^\circ$  respectively, whilst the pure acid used had  $[\alpha]_D -117.9^\circ$  in acetone.

(3) The contrast between the behaviour of *l*-menthyl *l*-mandelate towards aqueous- and ethyl-alcoholic alkali, respectively, as examined by one of us (T., 1904, 85, 1256) is highly significant. The mandelic acid recovered when the hydrolysis was carried out at  $100^\circ$  with the calculated quantity of aqueous alkali gave the value  $[\alpha]_D -126.4^\circ$  in aqueous solution, whereas with the calculated quantity of alcoholic potassium hydroxide at  $25^\circ$  the recovered acid had a much lower value, namely,  $[\alpha]_D -36.3^\circ$ . It was clear from these results, and also from others (for example, in the case of phenyl-*p*-tolylacetic acid), that there is more liability for racemisation occurring during the hydrolysis of esters by alcoholic alkali than by the action of alkali of the free acid. The important inference may be drawn that the active agent in promoting racemisation during the hydrolysis of an optically active ester by alcoholic alkali is the alkoxide rather than the hydroxide.

(4) In the course of their examination of the action of alkali on the diastereoisomeric *l*-menthyl phenyl-*p*-tolylacetates, McKenzie and Miss Widdows have pointed out that, when the ester of the *d*-acid was boiled for more than an hour with a slight excess of alcoholic potassium hydroxide, the hydrolysis was incomplete. The ester recovered from this action had, however, the value  $[\alpha]_D -54.7^\circ$  in acetone, whereas the pure ester with which the experiment was conducted had  $[\alpha]_D -53^\circ$ . Small as is the difference between these values, the conclusion that the original ester had undergone partial racemisation was justified. Here the racemisation causes an elevation of the optical rotatory power, inasmuch as the menthyl group in the ester is optically stable towards alkali. This observation is, so far as we are aware, the first example recorded of the catalytic racemisation of an optically active ester by alcoholic alkali. The partial conversion of *l*-menthyl *l*-diphenylsuccinate into *l*-menthyl *mesodiphenylsuccinate*, as observed by Wren and Still, has also a bearing on the same problem.

Extending the observations of Wren and Still (T., 1917, 111, 1019) on the formation of ethyl *mesodiphenylsuccinate* during the



# PROCEEDINGS

## OF THE

### CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, June 5th, 1919, at 8 p.m., Sir JAMES J. DOBBIE, D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society through the death of the following Fellows:

	<i>Elected.</i>	<i>Died.</i>
Thomas Fairley .....	May 18th, 1865.	Feb. 21st.
James Baird MacLachlan .....	May 4th, 1916.	May 25th.
Sir Boverton Redwood, Bart. ....	Jan. 18th, 1866.	June 4th.

Messrs. S. J. Hopkins, G. A. R. Kon, F. T. Stevenson, N. Singer, and H. G. Tribley were formally admitted as Fellows of the Chemical Society.

Certificates for election were read for the first time in favour of:

- William Barnes, 29, Conway Road, Luton.
- Frank Leslie Barrett, 46, Grantham Road, Horton, Bradford.
- Harold Ward Dudley, 10, Lanark Mansions, Maida Vale, W.9.
- Herbert William Gorbould, 45, Falmouth Avenue, Highams Park, E.4.
- Sampson Manson Hing, Y.M.C.A., Tottenham Court Road, W.1.
- Clive Newcomb, B.A., M.B., B.Ch., 48, Leigham Court Road, Streatham, S.W.16.
- Isaac Sklar, 29, Clark Street, Stepney, E.1.
- Colin Everett Spearing, Winslade, Eversfield Road, Reigate.
- Ernest Edward Wallen, 8, Glade Street, Bolton.
- Arthur Charles Vincent Weston, 24, Belsize Park Gardens, Hampstead, N.W.3.
- Harold Bishop Williams, 6, Hamlet Road, Upper Norwood, S.E.19.

The following papers were read:

- "An isotonic (isosmotic) apparatus for comparing molecular weights. Part I." By P. BLACKMAN.
- "The 'active substance' in the iodination of phenols." By V. COFMAN.
- "The chemistry of the glutaconic acids. Part XI. The occurrence of 1:3-addition to the normal form." By J. F. THORPE.
- "The formation and reactions of imino-compounds. Part XIX. The chemistry of the cyanoacetamide and Guareschi condensations." By G. A. R. KON and J. F. THORPE.

Ordinary Scientific Meeting, Thursday, June 19th, 1919, at 8 p.m., Sir JAMES J. DOBBIE, D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows:

	<i>Elected.</i>	<i>Died.</i>
Samuel Godfrey Hall .....	Feb. 16th, 1899.	June 9th.
Walter Parker .....	Feb. 5th, 1917.	April 15th.
James Fleming Stark .....	Dec. 15th, 1870.	June 13th.

It was announced that a communication had been received from the Committee of the Van't Hoff Fund for the endowment of research in pure and applied chemistry. The amount from this fund available for distribution during 1920 is about £140.

A Committee, consisting of Professor A. F. Holleman (President), Professor S. Hoogewerff, Professor A. Smits, and Professor E. H. Büchner (Secretary), has been appointed to award grants. Applications should be sent before November 1st, 1919, by registered post, to "Het Bestuur der Koninklijke Akademie van Wetenschappen: bestemd voor de Commissie van het 'Van't Hoff-fonds' Trippenhuis, Kloveniersburgwal, te Amsterdam." Every applicant is requested to submit a detailed account of the manner in which he proposes to expend the grant and to state the reasons for which he makes his application.

Papers embodying the results of the research may be published in any journal, but acknowledgment must be made of the source of the grant. Copies of papers containing the results of the research must be forwarded to the Committee.



Certificates were read for the first time in favour of:

Lawrence Eversley Campbell, B.Sc., 5, St. Matthew's Avenue, Surbiton.  
 Alan Ernest Gardiner, 21, Chestnut Road, W. Norwood, S.E.27.  
 Robert Grant, 24, Edward Street, Woollalua.  
 John Knaggs, B.Sc., South Street, Bridlington.  
 Charles Rose, B.Sc., 603, Chorley New Road, Horwich.

Certificates have been authorised by the Council for presentation to ballot under Bye-law I (3) in favour of:

Douglas Coghill, Kuala Lumpur, F.M.S.  
 Charles Edward Simithraaratchy, B.Sc., Trinity College, Kandy, Ceylon.

Messrs. H. E. Annett and A. J. Chapman were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared duly elected as Fellows:

Donald Bagley.	Denis Madden.
Edgar Beard, B.Sc.	Owen Leonard Maund.
Wilfrid Andrews Bell.	Brian Mead.
Alfred Randolph Campbell.	Rustom Jeejeebhoy Mistri.
Algernon George Crossley.	Charles Jean Stanislas Van Over-
Ananda Kishore Dás, M.A., B.Sc.	straeten.
Manik Lal Dey, M.Sc.	Arthur Pinkerton.
Philip Drinker, B.S.	Sidney Owen Rawling, B.Sc.
John Mouson Errington.	John David Smith.
Archibald Wooster Frame.	Sidney Albert Lewis Smith.
John William Gardom.	Cyril Richard William Stephenson,
Robert Stephen Glennie.	M.Sc.
Cecil Godfrey.	Arnold Teichfeld.
Sidney Herbert Hadfield.	Harold Toms.
Harry Harper, B.Sc.	Dudley Cloete Vining.
Herbert Hollings Jacques, B.Sc.	Edward John Wall.
Louis Charles Kemp.	William Wardlaw, M.Sc.
Herbert Joseph Seymour King, B.Sc.	Ernest Edward Whale, B.Sc.
Cyril Henry Stanley Kipping, M.A.	David Wingate.
Morvan Lapworth, B.Sc.	Arthur Samuel Wood, B.Sc.
Alexander Douglas Macallum, B.A.	Thomas Thorne Wood.
Ernest Neil Macallum.	George Ernest Yarrow, B.Sc.

The meeting was then adjourned and the Informal Meeting declared open.

## THE LIBRARY.

The Library will be closed for Stocktaking from Monday, August 11th, until Saturday, August 23rd, 1919, inclusive.

## LIST OF FELLOWS, 1919.

The List of Fellows for 1919 is now in active preparation, and changes of address received after July 31st cannot be included in it.

In order that the new list may be as complete as possible, those Fellows whose degrees and Christian names do not appear in full are requested to communicate them to the Assistant Secretary.

## ADDITIONS TO THE LIBRARY.

### I. *Donations.*

ATACK, FREDERICK WILLIAM, and WHINYATES, LEONARD [Editors]. The Chemists' Year Book, 1918—19. 2 vols. London 1919. pp. 1146. 15s. net. (*Reference.*)

From the Publishers: Messrs. Sherratt and Hughes.

FINDLAY, ALEXANDER. Osmotic pressure. 2nd edition. London 1919. pp. xi+116. ill. 6s. net. (*Recd.* 3/6/19.)

From the Publishers: Messrs. Longmans, Green and Co.

RICHARDSON, CLIFFORD. Papers on asphalt and asphalt pavements. (Together with one by E. C. PAILLER on The differentiation of natural and oil asphalt.) 1912—1917. (*Reference.*)

From the Author.

SENER, GEORGE. Outlines of physical chemistry. 7th edition. London 1919. pp. xx+432. ill. 6s. net. (*Recd.* 13/6/19.)

From the Author.

— A text-book of inorganic chemistry. 5th edition. London 1919. pp. x+621. ill. 7s. 6d. net. (*Recd.* 13/6/19.)

From the Author.

### II. *By Purchase.*

ABRAHAM, HERBERT. Asphalts and allied substances: their occurrence, modes of production, uses in the arts and methods of

testing. New York 1918. pp. xxv+606. ill. 25s. net. (*Recd.* 27/5/19.)

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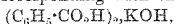
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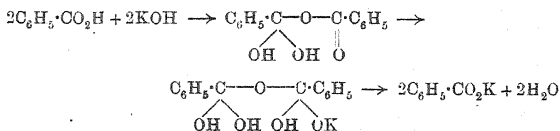
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has an augmented interest when viewed in relationship with the recent work of Dehn and Miss Merling (*J. Amer. Chem. Soc.*, 1917, **39**, 2646). Those authors claim to have prepared a number of compounds of potassium hydroxide with various organic acids, the addition having been conducted in the presence of anhydrous ether. Thus with benzoic acid a compound was isolated which, on analysis, gave figures corresponding with the formula



the scheme adduced being the following:



According to the same authors, compounds of potassium hydroxide with various esters can exist as definite entities, for example, the description of a compound consisting of molecular quantities of ethyl salicylate and potassium hydroxide is cited.

With those data at our disposal, we considered it desirable that an examination should be made in some detail of the behaviour on hydrolysis of an ester of an optically active monobasic acid of the type  $\text{R} \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H}$ , possessing a simple structure and with a high optical rotatory power. For this purpose, ethyl *l*-mandelate, which has  $[\alpha]_D -200.2^\circ$  in carbon disulphide solution, was selected.

First of all, the behaviour of *l*-mandelic acid towards potassium hydroxide in aqueous- and ethyl-alcoholic solutions, respectively, was examined under varied conditions of concentration and temperature. From the results recorded in table I (see experimental part), it was clear that aqueous alkali in the concentrations employed had only a very slight racemising action, even if used in considerable excess and at elevated temperature; moreover, alcoholic alkali caused racemisation, which was only slight at the ordinary temperature, but was pronounced when the alkali was in considerable excess at  $70.5^\circ$ .

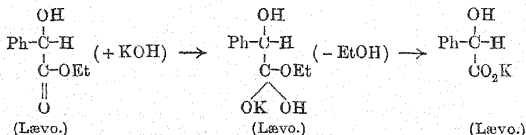
The complete hydrolysis of ethyl *l*-mandelate was next studied, the great difference in the extent of the racemisation when effected by alcoholic alkali as contrasted with aqueous alkali being clearly indicated (see table II).

The partial hydrolysis of the ester was next examined, and the rotation taken of the non-hydrolysed ester and of the mandelic acid resulting from the potassium salt formed. It appeared that the racemisation of the ester was more pronounced than that of the

acid, and the conclusion was reached that the ester was catalytically racemised. The specific rotatory power of the pure ester used was, as already stated,  $[\alpha]_D -200.2^\circ$  in carbon disulphide solution. In four separate experiments conducted with alcoholic alkali under different conditions, the ester which had escaped hydrolysis and was recovered gave the values  $[\alpha]_D -122.1^\circ$ ,  $-105.7^\circ$ ,  $-91.5^\circ$ , and  $-79.5^\circ$  respectively. Moreover, the effect was more noticeable at higher than at lower temperatures, and it was more extensive in alcoholic than in aqueous solutions; curiously enough, it was more marked with dilute than with concentrated alkali (see table III). The latter observation is interesting and worthy of further investigation; a satisfactory interpretation would doubtless be arrived at by a comparison of the velocity of hydrolysis with the velocity of racemisation in alcoholic solutions of varying concentrations.

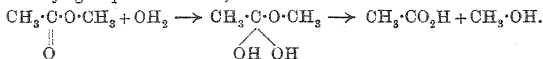
Finally, ethyl *l*-mandelate was hydrolysed by a moderate excess of alcoholic alkali, and the optical rotatory power of the non-hydrolysed ester and of the mandelic acid obtained from the potassium salt was examined at different stages of the hydrolysis. The recovered ester gave the values  $[\alpha]_D -162.8^\circ$ ,  $-120.2^\circ$ , and  $-69.6^\circ$  respectively in carbon disulphide. As we anticipated, the first portions of the ester to be hydrolysed gave a highly active acid, and the activity of the non-hydrolysed ester always lagged behind that of the acid formed (see table V).

The fact is accordingly established that the action of aqueous alkali on ethyl *l*-mandelate under the conditions quoted in the experimental part is accompanied with very slight racemisation, whereas with alcoholic alkali under similar conditions the racemisation is pronounced. The mechanism of these two actions must obviously be different, and we suggest that with aqueous alkali the following stages may occur:



If the additive compound depicted is formed as an intermediate phase, its existence is presumably only transient, the velocity of its formation being measurably slow as compared with the velocity of its decomposition, which we would suppose to be immeasurably fast. There does not appear to be anything in such an assumption which is opposed either to the bimolecular nature of ester-hydro-

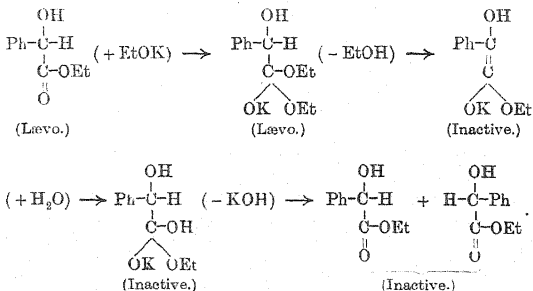
lysis or to the view held by some chemists that ionisation is the final effect instead of the initial cause of chemical reactions, and that association may precede ionisation even in aqueous solutions. A simple interpretation of this kind is not novel, recalling as it does the views advanced, for example, by H. E. Armstrong and Watson (*Proc. Roy. Soc.*, 1907, [A], 79, 579) with reference to the hydrolysis of methyl acetate by hydrochloric acid and nitric acid in the presence of certain salts. Whilst it is admitted by these authors that the hydrated acid is the effective hydrolyst, the assumption is made that water acts alone and attaches itself to the carbonyl group of the ester, thus:



On the basis of their results on the retarding effects of the inorganic salts on the velocity of hydrolysis, the same authors go so far as to assume that the salts actually enter into association with the ester, and consequently hinder to some extent the association of ester and hydrolyst.

Now, on the representation suggested above, ethyl alcohol separates from the additive compound in such a manner that the asymmetry of the molecule is still preserved, the elimination being effected from groups which are not directly attached to the asymmetric carbon atom. If the change proceeded entirely according to this scheme, the mandelic acid resulting from the potassium salt should be the pure levorotatory enantiomorph. In practice, however, the product is always racemised, although only slightly, and this is to be attributed mainly to the presence of a trace of potassium ethoxide formed from the alcohol eliminated. Although the equilibrated condition,  $\text{KOH} + \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{KO} \cdot \text{C}_2\text{H}_5 + \text{H}_2\text{O}$ , does not appear to have received the attention which its importance deserves, it is nevertheless certain that the quantity of ethoxide present during the hydrolysis of ethyl *l*-mandelate by aqueous alkali under the conditions examined by us can only be extremely small, sufficient, however, to induce the slight racemisation which is invariably observed. If it were feasible to select experimental conditions, of such an order that the ethyl alcohol would at the moment of its formation be removed from the sphere of action without being acted on by the potassium hydroxide, it should be possible to obtain the pure *l*-mandelic acid quite unracemised as the product of the action of the calculated amount of aqueous alkali on the ester. It has, however, to be recognised that under certain conditions racemisation can occur even when alcohol is absent.

On the other hand, since alcoholic potassium hydroxide contains potassium ethoxide, the more pronounced racemisation effects noted with alcoholic alkali are to be attributed to this factor. Here we suppose that the first phase of the action is an additive one, and that the formation of an unsaturated, unstable complex occurs after the additive compound has been formed, thus:



According to this picture, the asymmetry of the molecule is destroyed at the stage where the alcohol is eliminated, the ethoxide accordingly causing complete racemisation. A logical deduction would be that it should be possible to effect the complete racemisation of ethyl *l*-mandelate with potassium ethoxide if the experimental conditions could be so adjusted as to prevent the admission of potassium hydroxide into the system.

Wren's observations (T., 1918, 113, 215) on the action of aqueous-alcoholic alkali on methyl *d*-phenylsuccinate are in harmony with the above views. With the gradual addition of water to alcoholic alkali, the amount of hydroxide will increase, whilst the amount of alkoxide will diminish. Wren's results show clearly that the addition of water tends to check racemisation to a remarkable extent.

The fact that, when ethyl *l*-mandelate is hydrolysed by a quantity of alcoholic potassium hydroxide insufficient for complete hydrolysis the residual ester is partly racemised, would accordingly be interpreted in the following fashion. A portion of the pure ester is unattacked, whilst another portion is completely racemised by the potassium ethoxide; the ester which escapes being hydrolysed would, therefore, consist of a mixture of *d*- and *l*-esters containing an excess of the latter.

On the other hand, the following distinct reactions appear to





For the neutralisation of 0.38 gram of acid, 22.6 c.c. of 0.1105*N*-alkali are required. When a slight excess of alkali of this concentration was employed, there was still racemisation; the effect of raising the temperature is, however, clearly indicated, as also is the greater racemising effect of the alcoholic as contrasted with the aqueous alkali. The effects of the more concentrated alkali (0.93*N*) were more pronounced. Although the value  $-146.6^\circ$  obtained from the third experiment quoted in the above table is not far removed from that of the optically pure *l*-mandelic acid, the racemisation which occurred when the alcoholic solution was kept at the ordinary temperature and submitted to polarimetric examination at intervals was observed quite clearly, the  $\alpha_D$  falling from  $-1.21^\circ$  to  $-1.08^\circ$  ( $l=1$ ) after seven days. At  $70.5^\circ$ , the initial value for  $\alpha_D$  was  $-2.42^\circ$  ( $l=2$ ); after one hour  $\alpha_D$  was  $-2.15^\circ$ , and after three hours  $-1.92^\circ$ , whilst the acid recovered after the action had proceeded for thirteen hours had a value so low as  $[\alpha]_D -61.2^\circ$ . It must, of course, be noted that the alkali in this experiment was present in considerable excess. On the other hand, with aqueous alkali (0.93*N*), the initial value for  $\alpha_D$  was  $-2.89^\circ$  ( $l=2$ ); after three hours at  $70.5^\circ$ , the value had fallen to  $-2.80^\circ$ , and after thirteen hours to  $-2.45^\circ$ , whilst the recovered acid had  $[\alpha]_D -127.4^\circ$  after the action had been in progress for thirteen hours.

With regard to the conditions, the experiments quoted in the table are strictly comparable, as they were performed simultaneously.

*Complete Hydrolysis of Ethyl l-Mandelate by Potassium Hydroxide.*

The ester was prepared by esterifying the acid with ethyl alcohol and sulphuric acid. Its rotation was determined in carbon disulphide:

$$l=2, c=2.0155, \alpha_D^{20} -8.07^\circ, [\alpha]_D^{20} -200.2^\circ.$$

This value is higher than that quoted by Walden (*Zeitsch. physikal. Chem.*, 1895, 17, 708), who gives  $[\alpha]_D -180^\circ$  in carbon disulphide for  $c=2.5$ .

TABLE II.

Ester, grams.	Alkali.	Alkali required.	Conditions.	$[\alpha]_D$ of recovered acid.
0.697	35.5 c.c. alcoholic (0.1105N).	35.0 c.c.	3 days at ord. temp.	-86.0° ( $c=1.9$ )
0.697	35.5 c.c. alcoholic (0.1105N).	„	6 hours at 70°	74.5 ( $c=2.32$ )
0.789	80 c.c. alcoholic (0.1105N).	39.6	5 days at ord. temp.	93.7 ( $c=2.05$ )
0.789	80 c.c. alcoholic (0.1105N).	„	6 hours at 70°	80.6 ( $c=2.62$ )
1.0639	6.6 c.c. alcoholic (0.93N).	6.35	20 hours at ord. temp.	112.4 ( $c=3.16$ )
1.0639	6.6 c.c. alcoholic (0.93N).	„	3 hours at 70°	105.1 ( $c=3.07$ )
0.721	10 c.c. alcoholic (0.93N).	4.3	2 days at ord. temp.	118.4 ( $c=2.05$ )
2.0516	10 c.c. alcoholic (2.18N).	5.2	1½ hours at ord. temp.	124.1 ( $c=2.14$ )
0.5192	27 c.c. aqueous (0.1105N).	26.1	4 days at ord. temp.	149.4 ( $c=1.8$ )
0.5893	30.5 c.c. aqueous (0.1105N).	29.6	6 hours at 70°	152.2 ( $c=1.93$ )
0.9408	6 c.c. aqueous (0.93N).	5.6	1 day at ord. temp.	147.3 ( $c=2.99$ )
0.9008	5.8 c.c. aqueous (0.93N).	5.4	4 hours at 70°	146.5 ( $c=3.24$ )
0.6785	8.1 c.c. aqueous (0.93N).	4.0	2½ hours at 70°	144.8 ( $c=2.06$ )

Experiments with excess of hot concentrated alcoholic alkali were not performed, since the product would have been appreciably racemised by the alkali after the completion of the hydrolysis, and the value for the specific rotation would have varied according to the duration of heating.

Our thanks are due to Mr. Henry Wood, who in 1906 carried out the following experiments with the methyl and propyl esters of *l*-mandelic acid. A mixture of 3 grams of methyl *l*-mandelate and 50 c.c. of an aqueous solution of potassium hydroxide (1.114 grams, calculated 1.014 grams) was maintained at the ordinary temperature for seven days. The acid obtained gave the value  $[\alpha]_D -153.9^\circ$  for  $c=1.99$ . An experiment conducted under similar conditions with 3 grams of the ester and 48.5 c.c. of alcoholic potassium hydroxide (1.016 grams) gave an acid with  $[\alpha]_D -115.9^\circ$ . These results showed the difference between the behaviour of aqueous and alcoholic alkali. When propyl-*l*-mandelate was hydrolysed with a slight excess of aqueous alkali at the ordinary temperature, the acid recovered gave the value  $[\alpha]_D -149.4^\circ$ ; the behaviour of this ester towards alcoholic alkali was not examined at the time.

*Partial Hydrolysis of Ethyl l-Mandelate.*

(1) *With Ethyl-alcoholic Potassium Hydroxide (0.1105N).*—Ester, 3.7273 grams; 94 c.c. of alkali (calculated 187.3 c.c.). The solution was divided into two equal parts: (a) *At the ordinary temperature for forty-eight hours.*—The alcohol was removed from the neutral solution by evaporation, the residue added to water, and the non-hydrolysed ester extracted with ether and dried; its rotation determined in carbon disulphide solution was  $[\alpha]_D -105.7^\circ$  for  $c=2.19$ . The mandelic acid was obtained from the potassium salt in the usual manner, and its rotation determined in aqueous solution was  $[\alpha]_D -119.9^\circ$  for  $c=3.03$ . (b) *At  $70^\circ$  for four hours.*—Recovered ester,  $[\alpha]_D -79.5^\circ$  for  $c=4.69$ ; acid,  $[\alpha]_D -110.9^\circ$  for  $c=3.57$ .

(2) *With Ethyl-alcoholic Potassium Hydroxide (0.93N).*—Ester, 3.4658 grams; 10 c.c. of alkali (calculated 20.7 c.c.). The solution was divided into two equal parts: (a) *At the ordinary temperature for twenty-four hours.*—Recovered ester,  $[\alpha]_D -122.1^\circ$  for  $c=3.15$ ; acid,  $[\alpha]_D -131.3^\circ$  for  $c=3.37$ . (b) *At  $70^\circ$  for six hours.*—Recovered ester,  $[\alpha]_D -91.5^\circ$  for  $c=2.13$ ; acid,  $[\alpha]_D -122.1^\circ$  for  $c=2.31$ .

(3) *With Aqueous Potassium Hydroxide (0.93N).*—Ester, 3.4156 grams; 10 c.c. of alkali (calculated 20.4 c.c.). *At the ordinary temperature for three days.*—Recovered ester,  $[\alpha]_D -181.8^\circ$  for  $c=4.82$ ; acid,  $[\alpha]_D -152.2^\circ$  for  $c=2.02$ .

These results are contrasted in the following table.

TABLE III.

Alkali.		Ester hydro-lysed, t. per cent.	$[\alpha]_D$ of residual ester.	$[\alpha]_D$ of acid.	Race-misation of ester, per cent.	Race-misation of acid, per cent.
Alcoholic 0.1105N	Ord.	50.2	-105.7°	-119.9°	47.2	22.3
	70°	"	79.5	110.9	60.3	28.2
Alcoholic 0.93N	Ord.	48.3	122.1	131.3	39.0	15.0
	70°	"	91.5	122.1	54.3	20.9
Aqueous, 0.93N	Ord.	49.0	181.8	152.2	9.2	1.4

*Examination at Different Stages during the Complete Hydrolysis of Ethyl l-Mandelate by Alcoholic Alkali.*

The ethyl-alcoholic potassium hydroxide used was 0.202N. Six grams of the ester were dissolved rapidly at the ordinary temperature by shaking with 205 c.c. of alkali (calculated 165 c.c.). At intervals, 50 c.c. of the solution were withdrawn and run into a

slight excess of standard sulphuric acid, the solution being then titrated with standard alkali. In each case, the alcohol was removed by heating, and the ester and mandelic acid in the residue were separated as usual.

TABLE IV.

Interval.	Solution withdrawn.	Sulphuric acid, 0.998N.	0.202N-alkali required for excess of acid.
7 minutes	50 c.c.	10 c.c.	11.0 c.c.
25 "	"	"	23.0 "
65 "	"	"	33.9 "
1269 "	"	"	40.1 "

In table V, the specific rotatory power of the mandelic acid was determined in ethyl-alcoholic solution, the acid from which the ethyl *l*-mandelate was prepared having  $[\alpha]_D -152^\circ$  for  $c=1.671$  in ethyl alcohol.

TABLE V.

Fraction.	Ester hydrolysed, per cent.	$[\alpha]_D$ of ester recovered.	$[\alpha]_D$ of acid.	Ester racemised, per cent.	Acid racemised, per cent.
1	28	$-162.8^\circ (c=2.45)$	$-138.2^\circ (c=1.1)$	18.7	9.1
2	58	$120.2 (c=1.46)$	$119.0 (c=1.02)$	40.0	21.7
3	84	$69.6 (c=0.52)$	$104.3 (c=2.85)$	65.2	31.4
4	100	—	$96.3 (c=2.69)$	—	36.6

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## LI.—The Potential of a Nitrogen Electrode.

By FRANCIS LAWRY USHER and RAMAVENKATASUBBIER  
VENKATESWARAN.

THE decomposition potential of a normal solution of hydrazoic acid has been found by Le Blanc to be 1.29 volts, and this acid therefore resembles the halogen acids (except hydrofluoric) in furnishing at the anode an electromotively active substance the potential of which is lower than that of oxygen. The substance in question has been presumed to be ordinary nitrogen, so that it should be possible to construct a nitrogen electrode similar to a chlorine or a hydrogen electrode, and to measure its potential in a solution containing  $N'_3$  ions. An attempt which we have made to do this

has led to some interesting results, which leave little doubt that the substance set free at the anode in the electrolysis of azide solutions is not ordinary nitrogen, but an active form of it. Some purely chemical evidence in support of this conclusion was obtained by one of us in 1914, and it is proposed to resume these experiments as soon as circumstances permit; they are at present too incomplete for publication.

#### EXPERIMENTAL.

The *E.M.F.* of the combination  $N/10\text{-calomel}|N/100\text{-KCl}|N/100\text{-NaN}_3|N_2Pt$  was measured at  $30^\circ$ , the nitrogen employed being carefully freed from oxygen and oxides. The nitrogen electrode was about 0.4 volt negative to the calomel, and therefore slightly negative to hydrogen, a result which is clearly incompatible with the assumption that the nitrogen furnishes  $N'_3$  ions reversibly. It was, in fact, proved that the observed potential was unaffected by the presence of nitrogen. The attempt was repeated with several different kinds of electrode, but always with the same negative result.

Since the nitrogen liberated at the anode during the electrolysis of azide solutions is electromotively active, as shown by the existence of a definite decomposition voltage, it appeared probable that at the moment of its liberation it was different from, but was very rapidly converted into, ordinary nitrogen. It was therefore decided to polarise a platinum wire anodically in an azide solution with a definite *E.M.F.* in slight excess of the decomposition voltage, and to measure its potential, which would be slightly higher than the true potential corresponding with the reversible change  $N'_3 \rightleftharpoons$  active nitrogen. The electrolytic cell was made of paraffined teak-wood divided into three compartments by parchment paper diaphragms, the three compartments containing *N*-sodium azide, with some hydrazoic acid added to the middle compartment in order to neutralise any ammonia formed by reduction at the cathode. The potential of the anode was measured against a *N*/10-calomel electrode at the ordinary temperature ( $25\text{--}26^\circ$ ). The results read from the smoothed curves are shown in the following table. In Series I, about 5 cm. of platinum wire 0.5 mm. thick were used, in Series II about 2 mm. of the same wire, and in Series III a short point of very fine wire, the metal being well platinised in every case.

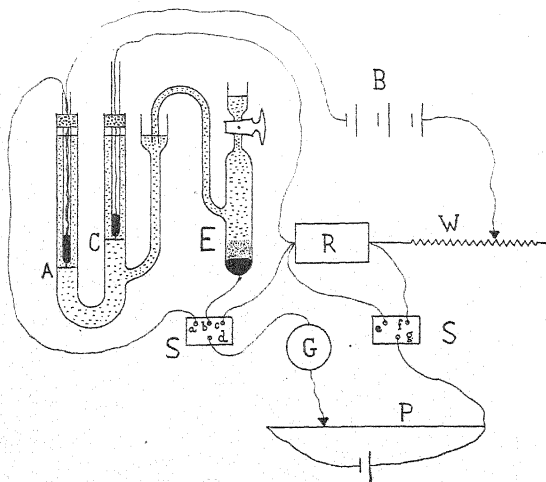
Applied <i>E.M.F.</i> Volts.	Potential of anode against <i>N/10</i> -calomel.		
	I.	II.	III.
1.20	0.690	0.760	0.788
1.30	0.698	0.770	0.800
1.40	0.704	0.782	0.813
1.50	0.712	0.797	0.829
1.60	0.722	0.812	0.843
1.70	0.732	0.830	0.861
1.80	0.743	0.848	0.880
1.90	0.754	0.873	0.904

Although the combination was so arranged that the potentials at the liquid junctions could be calculated after determining the transport number for sodium azide, it was unnecessary to do this, because, as is evident from the above table, a constant value for the potential of the nitrogen electrode was not obtained at any applied voltage. Its behaviour appears to be normal so far as the effect of increasing voltage is concerned, but depends on the size of the anode, that is, on the current density. The current flowing in the primary circuit was at all times sufficient to cause a brisk evolution of gas, so that the results cannot be attributed to want of saturation. With a view to investigate the relation between the potential and the current density, a series of measurements was made with varying but known current densities at a constant decomposing voltage.\* The arrangement shown diagrammatically in the accompanying figure was used. The solution of *N*-sodium azide, slightly acidified with hydrazoic acid, was contained in a tall U-tube with a side branch for the calomel electrode (*E*). The electrodes (*AG*) consisted of platinised platinum disks sealed into glass tubes which passed through corks, and could be moved up or down. The U-tube was tilted when in use in order to prevent an accumulation of gas under the disks. The electrolysing current was furnished by a battery (*B*), and passed through an adjustable low resistance (*W*), a resistance box (*R*), and the solution in the U-tube. *SS* are two paraffin block switches of which the terminals *d* and *g* were connected to a potentiometer (*P*), the other connexions being as shown in the diagram. In taking a series of readings, the circuit was first closed, *e* was connected to *g*, and *a* to *d*. Plugs were then taken out of the resistance box until the potential difference across the U-tube was approximately 1.31 volts (chosen as being slightly in excess of the decomposition voltage), and the rheostat (*W*) was then adjusted so that that figure was exactly attained. The second measurement was that of the fall of potential across the resistance box, and the third gave the *E.M.F.* of the combination nitrogen-

\* Keys, standard cell, and a buffer solution between the U-tube and calomel electrode are not shown.

calomel. The current flowing through the solution was known from the second measurement, which gave the fall of potential across a known resistance, and from this the current density was calculated, the area of the anode being always the same, namely, 0.65 sq. cm. By altering the position of the electrodes, the resistance of the solution could be varied, and therefore also the current density.

It was noticed that when the platinised electrodes were immersed in the solution, a slow evolution of nitrogen occurred even when no current was passed. This could not have been due to occluded



chlorine derived from the platinising liquid, since it took place after soaking the electrodes in ferrous sulphate solution and washing them thoroughly, but was probably due to catalytic decomposition by the platinum black. Shortly after this observation was made, we found that the phenomenon had already been studied by Oliveri-Mandalà (*Gazzetta*, 1916, **46**, ii, 137). The platinum apparently became "poisoned" after the evolution had proceeded for some time, and nitrogen ceased to be given off after the first series of readings had been taken. The following table shows the results obtained. The current density at the anode (C.D.) is given



in microamperes per sq. cm., and the *E.M.F.* of the combination in volts.

I.		II.		III.		IV.	
C.D.	<i>E.M.F.</i>	C.D.	<i>E.M.F.</i>	C.D.	<i>E.M.F.</i>	C.D.	<i>E.M.F.</i>
4707	0.446	4070	0.493	3659	0.508	3768	0.494
4838	0.468	4244	0.506	3738	0.524	3816	0.518
4975	0.482	4285	0.516	3831	0.542	3847	0.545
5136	0.497	4377	0.528	3893	0.558	3893	0.561
5444	0.520	4541	0.540	4019	0.577	3988	0.587
5741	0.541	4670	0.552	4112	0.593	4051	0.617
6131	0.564	4868	0.561	4237	0.608	4144	0.652
		4992	0.581	4364	0.629		
		5157	0.590				
		5362	0.615				
		5546	0.635				

If the above figures are plotted on a curve, it is seen that, as one would expect, the rate of increase of potential with current density diminishes as the latter increases. Since the potential is a measure of the concentration of the electromotively active substance in the electrode (assuming the solution to remain unaltered), it is evident that the latter is unsaturated even when nitrogen is being evolved freely, and one can only explain this behaviour by assuming that the  $N'_3$  ions furnish an active form of nitrogen on discharge, and that this is rapidly converted into ordinary nitrogen, probably catalytically by the platinum.

It has been shown in other instances that the velocity of reaction between a gas and a solid is proportional to the partial pressure of the gas. In the present case, the rate of formation of active nitrogen must be proportional to the current density, and its rate of decomposition may be considered proportional to its partial pressure, that is, to its concentration, of which the potential is a known function. If, therefore, the measurements correspond with a state of equilibrium (which they probably do, since the potential shows no variation so long as the current density remains constant),\* we obtain the relation: rate of formation of active nitrogen =  $k_1 D$  = rate of decomposition =  $k_2 C$ , where  $D$  is the current density and  $C$  the concentration of active nitrogen. If  $P$  is the measured *E.M.F.*, we get †  $P = a + b \log D$ , where  $a$  and  $b$  are constants. The following table shows the experimental values of the *E.M.F.* in Series II, the values read from a smoothed curve drawn through

\* In the four series of readings given, the actual values of the potential in the different series are not the same for a given current density. This variation is due to differences in the solutions, and is not observed in a solution of definite composition.

† By substituting  $C = k_1 D / k_2$  in the expression  $P = a + b \log c$ , and collecting the constant terms.

the figures enclosed in brackets, and the values calculated by means of this expression :

C.D.	E.M.F.		
	Measured.	Read from smoothed curve.	Calculated.
(4070)	(0.498)	(0.493)	(0.493)
4244	0.506	0.512	0.512
4285	0.516	0.516	0.516
4377	0.528	0.526	0.525
4541	0.540	0.542	0.542
4670	0.552	0.554	0.554
4818	0.561	0.568	0.568
4992	0.581	0.584	0.584
5157	0.590	0.598	0.598
(5362)	(0.615)	(0.615)	(0.615)
5546	0.635	0.630	0.630

The agreement between the observed and calculated figures is satisfactory, and probably indicates that the assumptions made are in the main correct. It is interesting to note that the above expression does not fit the curve obtained in Series I, where the solution was being decomposed catalytically during the observations, but that if a third constant (representing a constant additional supply of active nitrogen) is introduced, the agreement becomes good.

An attempt was made to obtain some idea of the rate at which the active nitrogen is decomposed in contact with the electrode. An azide solution was electrolysed in such a way that the gas accumulated in bubbles under the anode. On breaking the decomposing current, the potential fell at first so rapidly that it could not be followed, and dwindled to zero in about thirty seconds. A similar experiment with chlorine showed that the potential fell by 0.2 volt in twenty minutes, and a hydrogen electrode by 0.06 volt in the same time, so that the result with nitrogen cannot be explained by diffusion.

The only reference to any peculiarity in the chemical properties of the nitrogen obtained by electrolysing an azide appears to be in a paper by Browne and Lundell (*J. Amer. Chem. Soc.*, 1909, **31**, 435), who electrolysed a solution of potassium azide in anhydrous azoimide at  $-78^{\circ}$ , and, on the occasions when their apparatus was not shattered, observed that the gas evolved at the anode attacked mercury. Apparently, therefore, the active nitrogen is much less rapidly decomposed at a low temperature.

## LII.—*A Chemical Investigation of Banded Bituminous Coal. Studies in the Composition of Coal.\**

By FREDERICK VINCENT TIDESWELL and RICHARD VERNON  
WHEELER.

It is, and has been since pit-coal first became an article of daily use, a matter of common observation that any lump of bituminous coal taken haphazard is almost certain to exhibit, in a more or less marked degree, differences in the texture of its surface which give it a banded appearance, the bands being alternately dull and bright.

The subject of the banded appearance of bituminous coal has recently been treated in a more exact manner than heretofore by Stopes (*Proc. Roy. Soc.*, 1919, [B], 90, 470), whose observations can be briefly summarised as follows.

She distinguishes, not merely "dull" and "bright" bands, but four distinctive portions forming the mass of an ordinary bituminous coal. The four portions can be recognised and separated from each other both macroscopically and microscopically in thin sections. These four ingredients were provisionally named by Stopes:

- (i) Fusain. The equivalent of "mother-of-coal," "mineral-charcoal," etc., of various authors.
- (ii) Durain. The equivalent of "dull" hard coal of various authors; the "Matzkohle" of the Germans.
- (iii) Clarain. } Together the equivalent of "bright" or "glance" coal of
- (iv) Vitrain. } various authors; the "Glanzekohle" of the Germans.

These show various differences in character, and, in particular, markedly distinct microscopical features.

Microscopical and palaeobotanical study has thus been able to distinguish between four visible ingredients in banded bituminous coal, and to ascribe to each a character essentially different from the others as regards the appearance and probable nature of the materials of which it is composed. As a corollary to this work, we have undertaken to determine to what extent, or if at all, the four ingredients differ amongst themselves in their chemical nature as ascertained by ordinary methods.

So far as we are aware, the only previous detailed attempt to relate the texture with the chemical composition of a coal is that

\* The work by Dr. M. C. Stopes, the reference to which is given below, forms No. 1 of this series of researches.

by Grout (*Econ. Geol.*, 1911, 6, 449), who made a careful study of selected parts of a black lignite or sub-bituminous coal from Gorham Mine, Marshall, Colorado. Several references are to be found, it is true, to the difference in composition between a sample of "mother-of-coal" (fusain) and the coal with which it was associated; and there has been a tendency on the part of some writers to confuse fusain, which may occur in bands or layers, but is just as often present in coal in numerous very small pockets, with "dull" or "matt" coal (durain) (see, for example, Strahan and Pollard, *Mem. Geol. Surv. Engl. Wales*, 1915, 6, 91).

We do not propose to discuss the reason for the gross difference that undoubtedly exists between the chemical composition of fusain and that of coal, but to reserve such a discussion for a future memoir, since it belongs more properly to a disquisition on the mode of formation of the coal conglomerate. Our immediate concern is with the more subtle differences in composition that can be presumed to be correlated with the characteristic appearances of vitrain, clarain, and durain.

The coal chosen for this research was, for obvious reasons, one of those used by Dr. Marie Stopes for her investigations, namely, the Thick Coal, Hamstead Colliery. We are indebted to her for volunteering the task—a laborious one requiring much care—of providing supplies of each macroscopically distinct ingredient, free from the others, sufficient for chemical examination. The total supply was obtained from blocks of coal collected within a few cm. of each other in the same portion of the seam.

The fusain was obtained as a powder by scraping lightly with a knife at such cleavage surfaces as had wedges of the material on them. The durain was obtained as small blocks or broken bands by splitting off from it all bright streaks. To obtain the durain reasonably pure, it was necessary to split the coal considerably; although preponderatingly dull in appearance, a few bright streaks of hair-like fineness remained in it. In contrast to the brittle, powdery fusain, the durain is firm and hard.

Clarain preponderated in the sample. It is throughout banded finely with rather brighter and rather duller portions, but in general it has a subdued surface lustre when viewed broken at right angles to the bedding plane, which is distinct from the matt surface of the durain.

Vitrain is a conspicuous feature in a block of this coal. It was separated as small splints and cubes through the ready breaking up of its layers. The vitrain runs in horizontally extended bands varying from 1 to 6 mm. in thickness. Unlike the clarain, a single band does not show banding within itself, but the face at right

angles to the bedding plane is uniformly and brilliantly glossy, and instead of the usual cleavage the fracture tends to be conchoidal.

The methods of chemical investigation employed for each of the four ingredients have been: proximate and ultimate analysis; the action of solvents and of reagents; and destructive distillation in a vacuum, with examination of the gaseous and liquid products. A tabulation of the results obtained, so far as they admit of tabulation, is given later. Some description is first required of the different operations, further details of which are given in the experimental portion of the paper.

*The Action of Solvents.*—Extractions were made in Soxhlet fat-extraction apparatus, using from 1 to 10 grams of material ground so as to pass through a 200  $\times$  200 mesh sieve.

(1) *Pyridine:*

	Vitrain.	Clarain.	Durain.	Fusain.
Extract, per cent. on ash-free, dry coal .....	34.4	27.2	21.6	10.1
Colour of solution .....	Dark red.	Dark red.	Brownish-red.	Brown.

(2) *Chloroform Extraction of Pyridine Extract.*—One gram of each of the dried extracts of vitrain, clarain, and durain was extracted with chloroform during two days. Extraction appeared to be complete after twelve hours. The percentage of the pyridine extract soluble in chloroform was with vitrain 27, with clarain 30, and with durain 40.

From these results, the percentages of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -compounds present in the coal (see Stopes and Wheeler, "Monograph on the Constitution of Coal," 1918) can be calculated as follows:

	Vitrain.	Clarain.	Durain.
$\alpha$ -Compounds (insoluble in pyridine)...	65.8	72.8	78.4
$\beta$ -Compounds (soluble in pyridine, but insoluble in chloroform) .....	25.0	19.0	13.0
$\gamma$ -Compounds (soluble in both pyridine and chloroform) .....	9.2	8.2	8.6

Samples of vitrain and durain were extracted direct with chloroform and with ethyl alcohol; the percentages extracted are recorded in table V.

*The Action of Reagents.* (1) *Alcoholic Potassium Hydroxide.*—This reagent has been used by previous workers to determine the quantity of ulmin compounds present in a coal. The substances removed are no doubt ulmin compounds, but all such compounds are not necessarily soluble in aqueous or alcoholic potassium hydroxide (Stopes and Wheeler, *loc. cit.*); it is better, therefore, simply to record the fact that a certain portion of a coal is soluble in the

reagent, without attempting to draw any conclusion therefrom as to the total percentage of ulmin compounds present.

A modification of Hart's method of treatment (*Chem. Zeit.*, 1907, **31**, 640), in which the reagent is maintained at 80°, was used in the first instance, the results being:

	Vitrain.	Clarain.	Durain.
Soluble in hot alcoholic potassium hydroxide; per cent. on ash-free, dry coal .....	6.1	5.4	3.8

Stopes had observed that in the cold this reagent seemed to have a peculiar effect on vitrain, causing small lumps to "acquire the consistency of hard cheese or soap," so that thin flakes could be cut from it with a razor, whilst in untreated coal vitrain is hard and resistant to a cutting edge. It seemed desirable, therefore, to determine whether prolonged treatment of the powdered coals in the cold would result in greater quantities passing into solution. The percentages removed after eight weeks of such treatment were:

Vitrain.	Clarain.	Durain.
5.7	5.2	3.6

The softening or loosening action of the alkali observed by Stopes would thus appear to be caused by the removal of some binding material from the coal conglomerate; the ulmin compounds have been credited with a binding or cementing action.

(2) *Iodine*.—The absorption of iodine by coal may be regarded as giving an approximate measure of the proportion of unsaturated compounds present.

Before treating the four ingredients of banded coal, preliminary trials were made with other coals to determine the conditions of test most likely to yield accurate comparative results. These trials showed that iodine absorption by coal is very slow and may continue for a long time. It was, in fact, found to be impracticable to determine the maximum amount of iodine that can be absorbed by coal, for the absorption varied with the conditions, and more particularly with the length of duration of test. For example, Wijs' solution (iodine chloride in solution in glacial acetic acid), although causing about four times the absorption given by aqueous iodine, yet did not appear to be within measurable distance of giving a final value after twelve hours.

In recording the results that follow, it is necessary to distinguish between "permanent" and "temporary" absorption of iodine (see p. 635). The results given are strictly comparative, each of the four components of banded coal being treated under identical conditions.

TABLE I.

*Iodine Absorbed per cent. by Weight on Ash-free, Dry Coal.*

Duration of treatment.	Temporary. (Released on keeping.)				Permanent.				
	Hours.	Vitrain.	Clarain.	Durain.	Fusain.	Vitrain.	Clarain.	Durain.	Fusain.
1.	6.4	7.6	4.1	0.7	8.6	6.9	6.8	2.1	
3.	7.9	8.3	5.5	0.7	14.3	11.8	12.3	3.6	
6.	9.3	9.7	6.8	1.4	16.5	16.0	13.0	2.9	
24.	10.7	10.4	8.9	2.1	22.8	23.6	17.8	4.3	

These results were obtained with aqueous iodine ( $N/10$  in potassium iodide solution). With Wijs' solution, the following quantities of iodine, calculated as percentages on the ash-free, dry coals, were absorbed during six hours:

Temporary.				Permanent.			
Vitrain.	Clarain.	Durain.	Fusain.	Vitrain.	Clarain.	Durain.	Fusain.
18.6	20.8	17.1	8.6	67.9	63.2	51.3	4.3

*Destructive Distillation. Gaseous Products.*—The procedure adopted for the examination of the gaseous products was that of fractional distillation in a vacuum. In this manner, the ranges of temperature over which decompositions occurred, with the production of one or other of the usual constituents of coal-gas in predominant quantity, became manifest. With each of the four ingredients of banded coal, decomposition, as evinced by the evolution of gases in any quantity, did not become marked until a temperature of about  $350^{\circ}$  was reached, although slight decomposition occurred with each at a temperature of  $300^{\circ}$ . At  $200^{\circ}$ , with all except fusain, a trace of gas was evolved, together with a little liquid having an odour of light petroleum.

The tabulated results of the distillations are as follow:

TABLE II.

*Vitrain.*

Temperature .....	0-300	300-350	350-400	400-450	450-500	500-550	550-600°
Vol. of gas at N.T.P. evolved per gram of coal, c.c. ....	5.0	6.2	22.5	25.9	37.4	49.8	52.0
Analysis, per cent.							
$C_6H_6 + C_nH_{2n}$ .....	8.3	12.0	8.8	2.2	0.7	nil	nil
$CO_2 + H_2S$ .....	58.3	20.4	7.3	3.3	2.3	1.1	1.1
$O_2$ .....	0.5	0.4	nil	nil	nil	nil	nil
$C_2H_4$ .....	1.8	4.8	4.8	1.9	0.4	nil	nil
CO .....	21.7	20.8	14.8	15.1	15.0	11.3	12.1
$H_2$ .....	—	2.8	9.7	35.2	59.8	80.1	82.2
$C_nH_{2n+2}$ .....	8.0	38.8	55.1	42.3	21.8	7.5	4.6
Ratio C/A on explosion for paraffins .....	1.50	1.56	1.80	1.85	1.95	2.00	2.00

TABLE II. (*continued*).*Clarain.*

Temperature .....	0-300	300-350	350-400	400-450	450-500	500-550	550-600°
Vol. of gas at N.T.P. evolved per gram of coal, c.c. ....	4.5	5.4	19.8	23.0	35.0	35.7	50.0
Analysis, per cent.							
$C_6H_6 + C_nH_{2n}$ .....	9.0	10.0	9.0	2.3	0.9	nil	nil
$CO_2 + H_2S$ .....	58.5	24.5	10.6	6.3	4.0	1.4	1.3
$O_2$ .....	0.5	0.3	trace	nil	nil	nil	nil
$C_2H_4$ .....	1.5	4.2	4.6	2.0	0.3	nil	nil
CO .....	21.0	21.6	14.4	14.5	14.0	11.9	12.3
$H_2$ .....	—	3.0	9.3	33.0	58.5	76.0	80.0
$C_nH_{2n+2}$ .....	7.5	34.4	52.1	41.9	22.3	10.0	6.4
Ratio $C/A$ on explosion for paraffins .....	1.52	1.60	1.71	1.80	1.90	2.00	2.00

*Durain.*

Temperature .....	0-300	300-350	350-400	400-450	450-500	500-550	550-600°
Vol. of gas at N.T.P. evolved per gram of coal, c.c. ....	3.55	5.4	15.4	18.9	31.0	30.0	35.8
Analysis, per cent.							
$C_6H_6 + C_nH_{2n}$ .....	11.6	14.4	11.7	2.5	1.8	nil	nil
$CO_2 + H_2S$ .....	58.7	28.3	13.8	9.2	6.7	6.2	2.0
$O_2$ .....	0.6	0.4	0.1	nil	nil	nil	nil
$C_2H_4$ .....	1.0	3.3	4.3	2.1	0.3	nil	nil
CO .....	19.3	19.1	12.4	13.5	15.0	16.4	12.6
$H_2$ .....	nil	3.0	7.7	32.1	56.6	62.7	77.0
$C_nH_{2n+2}$ .....	7.3	29.8	50.0	40.6	19.6	14.7	8.4
Ratio $C/A$ on explosion for paraffins .....	1.40	1.45	1.70	1.85	1.95	2.00	2.00

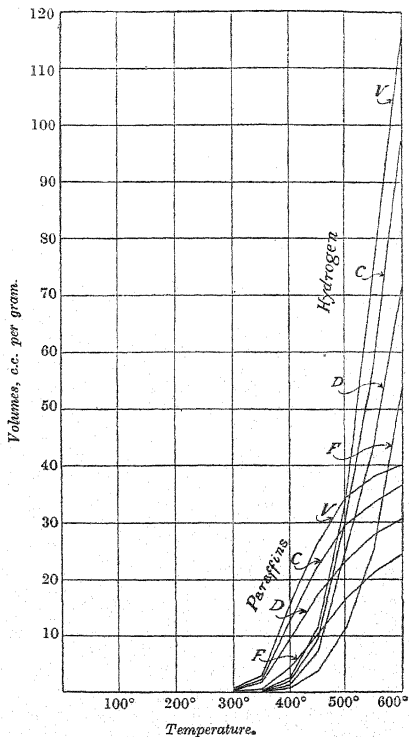
*Fusain.*

Temperature .....	0-300	300-350	350-400	400-450	450-500	500-550	550-600°
Vol. of gas at N.T.P. evolved per gram of coal, c.c. ....	1.8	2.0	7.5	12.0	17.5	22.0	35.0
Analysis, per cent.							
$C_6H_6 + C_nH_{2n}$ .....	11.5	8.9	7.5	2.8	1.8	0.7	nil
$CO_2 + H_2S$ .....	56.4	38.0	20.0	11.4	8.2	6.4	3.8
$O_2$ .....	nil	nil	nil	nil	nil	nil	nil
$C_2H_4$ .....	2.3	3.5	3.0	2.2	0.7	0.2	nil
CO .....	20.8	20.1	16.0	15.8	18.1	17.2	13.3
$H_2$ .....	nil	2.4	10.6	22.6	38.4	56.7	73.9
$C_nH_{2n+2}$ .....	3.0	23.0	42.3	45.2	32.8	18.5	9.0
Ratio $C/A$ on explosion for paraffins .....	1.25	1.42	1.60	1.82	1.90	2.00	2.00



In Figs. 1 and 2 are shown the volumes of individual gases plotted against the temperatures at which they were evolved. The

FIG. 1.



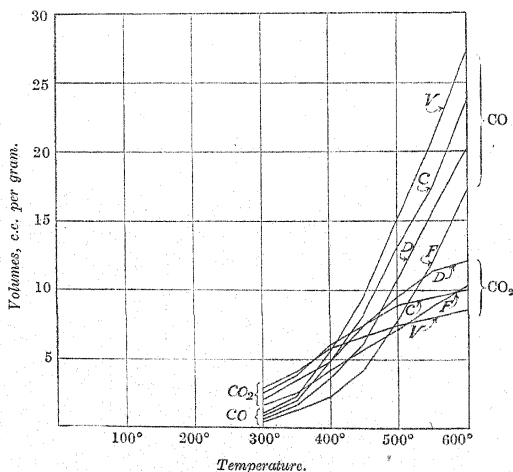
curves thus obtained show clearly the various stages of decomposition of the coal.

*Destructive Distillation. Primary Liquid Products.*—Only vitrain and durain were submitted to destructive distillation with

a view to examine the primary liquid products. Of fusain, an insufficient quantity was obtainable, whilst it seemed probable that the behaviour of clarain could be deduced from that of the other two components of banded coal, which would, at all events, afford the maximum degree of contrast. The records of the distillations are as follow.

*Vitrain. May 31st, 1918.*—The apparatus (see p. 636) having been exhausted of air, heating was begun at 2.0 p.m., the temperature being raised slowly to 100°. This temperature was main-

FIG. 2.



tained until noon on June 3rd. Water collected in the cooled receivers. *June 3rd.*—The temperature was raised gradually to 300°. Water and a little gas were evolved as the temperature increased. Oils began to appear at 300°. *June 4th.*—Increase of temperature was continued very slowly from 300° in order to determine the point at which active decomposition began. This was found to lie between 350° and 360°, over which range there was a rapid evolution of gas, water, and oils. Throughout the day the temperature was raised slowly to 400°. Viscid red oils began to appear at 390°, and their quantity increased with increased

temperature up to  $455^{\circ}$  (June 5th). *June 5th—7th.*—The temperature was raised, in stages of  $25^{\circ}$ , up to  $550^{\circ}$ . A rapid evolution of gas occurred at each successive increment of temperature, but there was no further appreciable production of oil or tar above  $460^{\circ}$ .

*Durain. June 14th.*—Heating begun, the temperature being raised slowly to  $100^{\circ}$ , and the water that was driven off collected. The temperature was maintained at  $100^{\circ}$  overnight. *June 15th—17th.*—Temperature raised to  $150^{\circ}$ ; very little more water was collected. Temperature raised slowly from  $150^{\circ}$  on the morning of June 17th; at 11.45 a.m., the temperature being  $250^{\circ}$ , water made a reappearance in quantity in the distillates; at 12.45 p.m., temperature  $300^{\circ}$ , oils began to collect in the receivers, but the evolution of gases was small. The rate of production of oils increased steadily with increased temperature without a corresponding increase in the quantity of gases; between  $350^{\circ}$  and  $360^{\circ}$ , the rate of evolution of gases increases slightly, but there was no marked decomposition point until the range  $370^{\circ}$ — $380^{\circ}$  was reached. *June 18th—24th.*—The sequence of events as the temperature was raised gradually to  $550^{\circ}$  was the same as with vitrain, except that a notable evolution of water occurred at  $450^{\circ}$ . As with vitrain, there was but little production of oil or tar above  $480^{\circ}$ .

The main products of the distillations, calculated as percentages, by weight, on the ash-free, dry coals, may be tabulated as follows:

TABLE III.

	Vitrain.	Durain.
Residue (ash-free) .....	79.0	79.0
Water of decomposition ...	6.7	5.8
Tar and oils .....	5.6	8.0
Gas (by difference) .....	8.7	7.2

From the tar and oils there were obtained on distillation:

Oils .....	3.6	4.0
------------	-----	-----

The oils were composed of:

Phenols .....	2.2	1.6
Neutral oils.....	1.4	2.4

The residue remaining in the retort in each instance consisted of loose particles little different in appearance from the original materials. With durain there were slight indications of coherence of some of the particles; no coherence could be observed with vitrain. With the latter there was a shrinkage in volume amounting to about 25 per cent. of that of the original coal; with the former, the shrinkage was only about 10 per cent.

*Examination of the Liquid Distillates.*—Owing to the small quantities obtained, it was not possible to make a complete examination of the fractions collected at different temperatures. Up to 150°, with both vitrain and durain, the distillates consisted of water; both were neutral and colourless and free from oils and organic or mineral salts.

The distillates obtained between 150° and 300° were aqueous, with traces only of hydrocarbon oils. They fumed strongly in air, and were found to be concentrated solutions of hydrochloric acid. There was evidence of the presence of compounds of the polyphenol type in traces.

The aqueous portions separated from the distillates between 300° and 500° were also strongly acid (hydrochloric acid). On adding excess of potassium hydroxide, the vitrain distillate evolved an inflammable gas, strongly alkaline and with an odour like that of methylamine, whilst the durain distillate evolved a strongly alkaline gas, not unlike pyridine in odour. No ammonia could be detected in either distillate. Colour reactions for polyhydric phenols were again noted.

The method of examination of the tar and oils was, for both vitrain and durain, to mix together the fractions obtained at different temperatures and distil them under reduced pressure. The oils obtained were treated with solutions of sodium carbonate and potassium hydroxide to remove phenols, with hydrochloric acid to remove traces of bases, and finally with water. The phenols were liberated from their alkaline solution and distilled, as were the neutral oils. The results are best shown in parallel columns.

TABLE IV.

Vitrain.	Durain.
Below 250° (40 mm.) 64 per cent. of the tar distilled without decomposition. At 250° decomposition began. The oils that passed over at that temperature began to solidify on cooling.	Below 300° (25 mm.) 60 per cent. of the tar distilled without decomposition. Above 260° the oils coming over began to solidify on cooling. At 300° decomposition began with evolution of HCl.
	The oils were poured off from the solid distillate.

Examination of the oils showed:

	Vitrain.	Durain.
Soluble in dilute Na <sub>2</sub> CO <sub>3</sub> solution .....	10 per cent.	} 40 per cent.
Soluble in 15 per cent. KOH solution ...	50 "	
Soluble in HCl .....	traces	traces
Neutral oils .....	40 per cent.	60 per cent.

TABLE IV. (*continued*).

Examination of the phenols showed:

Vitrain.	Durain.
The sodium carbonate solution contained polyphenols ( <i>o</i> -dihydroxy). The phenols liberated from the potassium hydroxide solution gave on distillation:	The total phenols on distillation gave:
(1) 50 per cent. boiling at 200–212°.	(1) 25 per cent. boiling at 200–220°.
(2) 25 per cent. boiling at 260–280°.	(2) 25 per cent. boiling at 240–280°.
(3) 25 per cent. residue.	(3) 50 per cent. residue.
Fraction (1): C=76.96; H=7.76. D <sub>15</sub> <sup>15</sup> 1.025.	Fraction (1): C=78.49; H=8.67.
Fraction (2): C=78.12; H=7.70. Very viscous.	Fraction (2): C=80.86; H=7.91. Very viscous.

Examination of the neutral oils showed:

Vitrain.	Durain.
Distilled almost completely at 160–320°.	Distilled almost completely at 160–340°.
C=85.86; H=9.91 (C+H=95.8).	C=85.44; H=10.39 (C+H=95.8).
	Charring with cold sulphuric acid left only about 10 per cent. of saturated hydrocarbons.

It will be noticed that the phenols derived from both coals fall into two well-defined groups, the first distilling at 200–220°, the second at 240–280°. The first group, in their constants and analyses, in their colour reactions with ferric chloride and other salts (aqueous and alcoholic), and in their phthalic anhydride condensations, agreed with the lower simple phenols, and were presumably cresols and xylenols. There was evidence also of the presence of some more complex phenol, or phenol ether, perhaps guaiacol. The second group gave pronounced colour reactions of the polyhydric phenols, and more particularly of the *o*-dihydroxybenzenes, but probably consisted mainly of condensed products. Protocatechuic acid, or a similar compound, was present in the washings from the phenols before their final distillation. This decomposes normally at about 200°, but may easily have escaped decomposition under the conditions of the distillations. Durain gave a more complex mixture of phenols than vitrain.

The distilled neutral oils from both coals were very similar, yellowish-brown oils. They did not consist exclusively of hydrocarbons, and the proportion of saturated hydrocarbons was low.

Paraffin wax was obtained in quantity from the higher boiling fractions of each tar.

The general analytic results can be summarised as follows:

TABLE V.

	Vitrain.	Clarain.	Durain.	Fusain.
Density .....	1.290	1.280	1.395	—
<i>Ultimate analysis.</i> —Per cent. on ash-free, dry coal:				
Carbon .....	78.5	79.1	80.8	84.7
Hydrogen .....	5.15	5.2	5.1	3.9
Oxygen .....	13.9	13.4	11.8	9.7
Nitrogen .....	1.33	1.28	1.3	1.05
Sulphur .....	1.12	1.02	1.0	0.65
<i>Proximate analysis:</i>				
Moisture, per cent. ....	12.6	10.2	6.5	3.9
Ash, per cent. ....	1.2	1.45	3.6	10.0
Volatile matter, per cent. on ash-free, dry coal .....	38.6	40.8	39.4	22.6
<i>Extractions.</i> —Per cent. on ash-free, dry coal:				
By pyridine .....	34.4	27.2	21.6	10.1
By alcohol .....	6.6	5.7	3.1	—
By chloroform .....	2.85	—	2.4	—
Pyridine extract soluble in chloroform, per cent. ....	27.0	30.0	40.0	—
Percentages of $\alpha$ -, $\beta$ -, and $\gamma$ -compounds in the coal:				
$\alpha$ -Compounds .....	65.8	72.8	78.4	—
$\beta$ - " .....	25.0	19.0	13.0	—
$\gamma$ - " .....	9.2	8.2	8.6	—
<i>Action of reagents.</i> —Per cent. on ash-free, dry coal:				
Solubility in alcoholic potassium hydroxide:				
(1) Hot .....	6.1	5.4	3.8	—
(2) Cold .....	5.7	5.2	3.6	—
Iodine absorption (permanent):				
N/10-aqueous iodine, in 24 hours .....	22.8	23.6	17.8	4.3
Wijs's solution, in 6 hours .....	67.9	63.2	51.3	4.3

The general impression created by an examination of the results recorded in this table is of a gradation of properties as we pass from vitrain to durain. Fusain, as already noted, stands apart in its character from the other three ingredients of banded coal. The ultimate analyses show a steady rise in carbon and fall in oxygen content in the order (1) vitrain, (2) clarain, and (3) durain, and this order is maintained with practically every property investigated.

Thus there is a regular reduction in moisture content and increase in ash content. The marked retention of moisture by vitrain most probably results from its colloidal nature, indicated by the conchoidal fracture and the absence of any recognisable structure. The ash content may to a certain extent affect the surface lustre of the coal. Indeed, from chemical examination alone, one might be tempted to say that durain is durain because it is rich in ash; but it is clear from the work of Stopes that the decisive factor affecting the lustre is the presence or absence of plant structure. No doubt there is a direct connexion between the ash content of a coal and the presence of plant remains therein.

The results of extractions both by organic solvents and by alcoholic potassium hydroxide exhibit well the gradation in properties from vitrain to durain; they also suggest a lack of homogeneity in vitrain not evident from microscopical examination. The fact that both vitrain and durain (and, it may be assumed, clarain also) contain nearly the same proportions of  $\gamma$ -compounds is striking. The chief difference between the ingredients of banded coal, as revealed by the action of pyridine and chloroform, lies, therefore, in the amounts of  $\alpha$ - and  $\beta$ -compounds present. If, as has been suggested, the action of pyridine is mainly a mechanical loosening of the structure of the coal conglomerate, the  $\alpha$ - and  $\beta$ -compounds may actually be, as from their chemical behaviour they appear to be, essentially similar in character. From this point of view, the main difference between vitrain and durain would be a physical one, and would lie in the ease with which their (colloidal?) structures are disintegrated. The fact that the action of chloroform direct on the coals is to remove much smaller proportions of soluble matter than when an attack is first made with pyridine is in agreement with this suggestion.

Alcohol appears to dissolve a portion of the coal conglomerate unaffected by chloroform—possibly the “resins,” using the word in its strictest sense. It is noteworthy that the proportions dissolved are higher than is usual with bituminous coals.

Perhaps the most striking evidence of gradation in properties of the four ingredients is afforded by the destructive distillations with examination of the gaseous products (see table III and Figs. 1 and 2). The volume-temperature curves obtained for the individual gases run nearly parallel, each to each, there being a rapid evolution of paraffins beginning at 350° and of hydrogen beginning at 400°.

The quantities of each gas (carbon dioxide excepted) evolved over equal temperature ranges are greatest with vitrain and least with fusain, clarain and durain occupying intermediate positions.

The analyses of the gases evolved from each at any given temperature interval are very similar; it is their quantity that differs. The difference between the coals—between vitrain and durain, for example—is therefore not such as exists between  $\alpha$ - $\beta$ - and  $\gamma$ -compounds, which yield distinctive gaseous mixtures on destructive distillation, the former being rich in hydrogen and the latter rich in paraffins (Clark and Wheeler, T., 1913, 103, 1704). The parallel volume-temperature curves show that for each of the four components of banded coal the relative production of hydrogen and paraffins is approximately the same, indicating that each contains similar proportionate amounts of the two characteristic ingredients of coal, namely,  $\alpha$ - and  $\beta$ -compounds (regarded together as being similar in their behaviour on destructive distillation) and  $\gamma$ -compounds.

For carbon dioxide, the same order is preserved up to 400°, but is reversed at higher temperatures. With fusain, the evolution of carbon dioxide is constant for each interval of 50° between 350° and 600°.

On comparing the records of the distillations conducted on a larger scale with vitrain and durain, it will be seen that in general durain required higher temperatures to resolve it. Vitrain had a well-defined decomposition point at 350–360°, with a rapid evolution of gas and oil, whilst the decomposition point of durain was less well marked at 370–380°. Moreover, all the tar obtainable from vitrain had distilled over before a temperature of 460° was passed, whereas with durain tar was still produced at 480°.

Vitrain yielded less tar than durain, the same amount of residue, but more water of decomposition and more gas. The tar from vitrain yielded less pitch than that from durain, the quantity of oils finally obtained from the two coals being nearly the same. A difference between the distillates further appears in the character of the oils.

The high proportion of phenols in the tar oils, and the oxygenated character of the neutral oils, which contained but little saturated hydrocarbons, is noteworthy. Jones and Wheeler (T., 1914, 105, 140) found from 12–15 per cent. of phenols in the tar oils from a Durham bituminous coal, and later (T., 1915, 107, 1318) showed that these were produced exclusively from the "cellulosic" ( $\alpha$ - and  $\beta$ -compounds) portion of the coal. The large proportion of phenols in the tar oils from the Hamstead coal used in the present research (50 per cent.) is due to the nature of the coal, which is highly oxygenated (10–13 per cent. of oxygen), a fact which also accounts for the oxygenation of the neutral oils.

It is not possible in the present state of ignorance of the chemical



composition of coal to draw precise conclusions regarding any difference in constitution that may exist between vitrain, clarain, and durain. The chemical data obtained point to the differences that might be expected to accompany the obvious difference in physical character being of degree rather than of kind. No characteristic reaction or behaviour for any one of the components of banded coal, such as might be expected were there a fundamental difference in the chemical composition of the coals, was disclosed.

The analytical results indicate for clarain a composition approximately one-third the way between vitrain and durain. It is interesting to find, therefore, that as we pass from vitrain to durain, the "reactivity" of the coal (that is to say, the extent of its susceptibility towards solvents and reagents) diminishes in the ratio vitrain:clarain:durain=1:0.9:0.7. This relationship applies also to the results of destructive distillation (except as regards the proportions of carbon dioxide evolved).

Such a relationship can be explained on the assumption that the coals are composed of a "reactive" group of compounds, together with a relatively "inert" material. The former alone is attacked by solvents, responds to reagents, and yields the main bulk of the gases and tars on distillation. The latter is chiefly responsible for the evolution at the higher temperatures of carbon dioxide on destructive distillation, and perhaps also for the neutral oils. It is clear, also, that the "reactive" group of compounds must contain more oxygen and less carbon than the "inert."

On this assumption, vitrain, clarain, and durain are similar as regards the composition of the "reactive" material they contain, as is shown by the approximate constancy of the ratios of "reactivity," but differ in the proportions of "reactive" and "inert" constituents they contain; it is conceivable, also, that the character of the latter varies, though a consideration of the ultimate and proximate analyses of the three ingredients does not point to this being so.

#### *Summary.*

In the banded Hamstead coal investigated, the ingredients (leaving out of account fusain) show differences which grade them in the sequence vitrain, clarain, and durain. This sequence is evidenced in the fall in the moisture- and rise in ash-content; in the increase of carbon- and decrease of oxygen-content; and in the diminishing "reactivity" towards solvents, reagents, and heat treatment.

Whilst making clear interesting differences which would scarcely

have been expected from portions of coal so immediately adjacent in the same seam, the work has not revealed the presence of essentially distinct types of chemical compounds peculiar to any one of the ingredients of banded coal.

That portion of each ingredient responsible for the reactions observed appears to be of nearly constant composition. It is suggested that the difference between the ingredients lies in the proportion of "inert" or unresponsive material with which this "reactive" portion is associated. If a given weight of vitrain be assumed to contain  $x$  parts by weight of "reactive" material, the same weight of clarain would contain  $0.9x$  and of durain  $0.7x$  parts.

Correlation of the microscopical with the chemical and other data available respecting banded bituminous coal is reserved for a future communication.

#### EXPERIMENTAL.

The various operations were conducted throughout under conditions strictly comparative for the four ingredients of the banded coal.

*Analyses.*—For the proximate analyses, the methods recommended by the American Chemical Society were employed. The ultimate analyses were made in the usual manner, sulphur being determined by Eschka's and nitrogen by Kjeldahl's method. For the estimation of carbon and hydrogen, the combustion tube was packed with copper oxide and lead chromate. The four ingredients differed considerably in their behaviour during combustion, fusain burning with difficulty in oxygen, whilst the combustion of vitrain became uncontrollable, showers of sparks being produced. With the latter, it was found necessary to start the combustion very slowly in a stream of air, and only to use oxygen towards the end of the operation. In each instance, the result recorded is the mean of several concordant determinations.

Each sample used for combustion analysis was dried in air during one hour at  $105^{\circ}$ . Experiments at present in progress on the rates of oxidation of the coals show that such drying would have the effect of raising their oxygen content and lowering their carbon content by less than 0.1 per cent.; moreover, the amount of alteration is approximately the same for each ingredient of the banded coal.

*The Action of Solvents.*—The extractions with organic solvents were made in all-glass Soxhlet apparatus, the coals being enclosed in thimbles of filter paper or alundum and held in place by plugs

of glass wool. Extraction was continued until the solvent passed over colourless, and generally for as long again. The coals were stirred at intervals, and fresh charges of solvent used from time to time. The solution obtained was filtered and distilled, and the extract freed from the last traces of solvent by evaporation on a watch-glass in a vacuum or in a stream of nitrogen, being finally allowed to remain during several weeks in a vacuum over sulphuric acid.

The coals were air-dried (at  $105^{\circ}$ ) for the pyridine (1 gram), dried at  $105^{\circ}$  in the absence of air for the pyridine-chloroform (10 grams), and undried for the alcohol and chloroform (5 grams) extractions. The solvents were dry and redistilled.

*The Action of Reagents.*—Extractions with alcoholic potassium hydroxide were made thus: (1) One gram of coal was heated with 25 c.c. of 0.7*N*-potassium hydroxide in absolute alcohol at  $80^{\circ}$  during eight hours. The solution was diluted with water and filtered, and the alcohol evaporated. The "ulmin compounds" were then precipitated by concentrated hydrochloric acid, filtered from the solution, washed with distilled water, dried at  $105^{\circ}$ , and weighed. (2) For extraction in the cold, 1 gram of coal was allowed to remain during eight weeks in contact with 25 c.c. of 4*N*-potassium hydroxide in 75 per cent. alcohol, with frequent shaking. The amount of extracted matter was determined as in (1).

Iodine absorptions were determined by two methods. (1) The coal, weighing 0.1 gram, was placed in a 250 c.c. stoppered bottle with 25 c.c. of *N*/10-iodine in aqueous potassium iodide solution. The bottle was then shaken mechanically during the required time. The residual iodine was titrated with *N*/10-sodium thiosulphate solution (leaving the coal in suspension), using starch as indicator. (2) Iodine chloride in solution in glacial acetic acid was employed in place of aqueous iodine, using 10 c.c. of *N*/5-solution with 0.1 gram of coal.

Preliminary work with different coals showed that a considerable proportion of the iodine removed from solution by the coal was evolved on keeping in contact with sodium thiosulphate solution. This evolution was not affected to an appreciable extent by the acidity of the solution, and appeared to be of iodine merely adsorbed by the coal. The adsorbed iodine was determined by adding definite volumes of sodium thiosulphate solution in excess at intervals until no further evolution could be detected, the final titration being made at the end of twenty-four hours.

*Destructive Distillation. Gaseous Products.*—The method of experiment and apparatus were as described by Burgess and

Wheeler (T., 1911, 99, 639), except that 1 gram only of coal was employed without admixture with sand.

*Liquid Products.*—The general arrangement of apparatus and method of carrying out the distillations were similar to those employed by Jones and Wheeler (T., 1914, 105, 140). In the place of the spherical retort used by them, a cylindrical vessel of Jena glass, 4 cm. in diameter and 14 cm. long., was employed. This form of retort allowed of a more rapid equalisation of temperature throughout the mass of the coal than the spherical form, and permitted, in consequence, more rapid distillation. The coal (about 200 grams in weight) with which the retort was completely filled was undried, and was sieved so as to pass through a 10 and remain on a 60 mesh sieve. It was held in position, when the retort was inverted during the distillation, by a plug of glass wool.

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### LIII.—*The Rotation-dispersion of Butyl, Heptyl, and Octyl Tartrates.*

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ANOMALOUS rotation-dispersion is exhibited by comparatively few optically active compounds in the homogeneous state; such compounds may be conveniently classified into (1) those containing one asymmetric carbon atom, (2) those containing more than one asymmetric carbon atom, and (3) those having an absorption band in the visible part of the spectrum.

The first two of these classes and certain members of the last class exhibit a remarkable similarity in the influence which temperature and solution have on their rotation-dispersion. By examination of the circumstances in which these compounds exhibit anomalous rotation-dispersion, it is seen that in all cases *the compound becomes, or tends to become, normal in its rotation-dispersion the farther its rotation is removed from the line of zero-rotation* by the effects of temperature or dilution in solution; that is, in all cases the anomaly occurs relatively\* near to the line of zero-rotation.

\* A high temperature-coefficient or dilution-coefficient is thus essential to the occurrence of the anomaly.

Much use has been made in recent years of the so-called "characteristic diagram" of Armstrong and Walker (*Proc. Roy. Soc.*, 1913, [A], 88, 388) for representing the phenomena of rotation-dispersion. Such a diagram for *n*-butyl tartrate is drawn in Fig. 1A, in which are set out the specific rotations for different temperatures for the wave-lengths 4861, 5461, 5893, and 6708. It may be pointed out that in such a diagram a line is drawn at  $45^\circ$  to the line of zero-rotation, and on this line the rotation values for wave-length 5461 (mercury-green) are set out. Thus, for any given temperature, the position of the rotation value for  $\lambda$  5461 is found on this line, and on a vertical ordinate through this point are marked the rotations at the same temperature for the other wave-lengths. After proceeding in the same way for observations made at other temperatures, the points representing the specific rotations for each wave-length are joined up by lines, which are found to be approximately straight and to intersect either in a single point or in a series of points near the line of zero-rotation.

In the above case of butyl tartrate, it will be seen that the points representing the rotations at the higher temperatures do not fall on their respective wave-length lines. This divergence is due to the maximal values for specific rotation being reached at different temperatures for different wave-lengths. The points for each wave-length thus cease to lie on a straight line when the neighbourhood of the maximum rotation is reached. Thus, in Fig. 1A especially is this the case for  $\lambda$  5893 and 6708. Of course, all values for  $\lambda$  5461 (mercury-green) lie by definition on the line drawn at  $45^\circ$  to the zero-line.

It is obvious that the same diagram may be used for similarly recording changes in rotatory dispersion brought about by solution and other influences, besides that of temperature.

The characteristic diagram, which thus serves to correlate the rotatory powers of many derivatives of similar constitution or of the same parent substance, has been successfully used by Pickard and Kenyon (T., 1914, 105, 843) to predict the conditions under which  $\beta$ -octyl acetate would exhibit anomalous rotation-dispersion.

For most, if not all, of the substances described by Pickard and Kenyon, the characteristic diagram represents lines (for  $[\alpha]_{4359}$ ,  $[\alpha]_{5461}$ ,  $[\alpha]_{5893}$ , and in some cases  $[\alpha]_{\text{mercury-yellow}}$ ) which do not intersect on the line of zero-rotation, but at some distance either above or below this line. If, therefore, the characteristic diagram is really indicative of the optical properties of the compounds of which the rotation values are plotted, then, obviously, all these compounds must have anomalous rotation-dispersion when the rotation assumes a value falling between zero and the value of the rotation at the

point of intersection of these lines. Pickard and Kenyon, adopting the hypothesis of Armstrong and Walker that anomalous rotation-dispersion is always due to the presence of dynamic isomerides, ascribe the anomaly in the rotation-dispersion of some of the compounds studied by them to the fact that "the esters at low temperatures, and methyl- $\alpha$ -naphthylcarbinol at high temperatures, are, or tend to become, really homogeneous, as the conditions of temperature favour the existence of one only of the two isomeric forms, which have been assumed to be present" (T., 1914, 105, 1119). As a corollary of this, it would therefore follow that when optically active compounds assume rotation values between zero and that of the intersection point on the characteristic diagram, two dynamic isomerides are present.

As already pointed out by Patterson (*Trans. Faraday Soc.*, 1914, 10, 74), however, the values of the rotation in the characteristic diagram "do not necessarily have anything whatever to do with the presence or absence of dynamic isomerides"; the characteristic diagram is, in fact, a convenient method of plotting the rotation values for different wave-lengths against the rotation value for a particular wave-length. It thus affords a test as to whether the dispersion-coefficient  $\Delta[\alpha]_{\lambda_1}/\Delta[\alpha]_{\lambda_2}$ \* (Winther, *Zeitsch. physikal. Chem.*, 1903, 45, 373) is constant during the variation of the rotation, which may be brought about by (1) changes in the concentration of the active compound in solution, (2) changes of temperature, (3) changes of solvent, (4) changes caused by the combination of the active compound, and (5) changes caused by the substitution of one member of a series for another (really a special case of No. 4). By means of this method, in fact, a number of isolated observations, made under varied conditions, may be co-ordinated in one diagram.

The "rational zero," advocated by Patterson (T., 1916, 109, 1176), when used for calculating the dispersion-coefficient gives much more constant values than if the zero of rotation is used for this purpose. Moreover, the main features of the characteristic diagram are actually summarised by the values of the rational zeros and the rational dispersion-coefficients.

In the case of a single optically active compound, the characteristic diagram, in part, eliminates the *accidental* condition of the compound. On the same diagram may be co-ordinated the rotation values for different wave-lengths for a compound at different temperatures, in various concentrations, in different solvents, and

\*  $\Delta[\alpha]_{\lambda_1}$  and  $\Delta[\alpha]_{\lambda_2}$  are the corresponding changes produced in the rotation for the wave-lengths  $\lambda_1$  and  $\lambda_2$  respectively, by varying the condition of the active compound.

even in some cases in different states of combination; thus the characteristic diagram does seem to justify its name.

Compounds, the characteristic diagram of which approach the ideal represented by the lines for different wave-lengths crossing at the same point, have always normal rotation-dispersion; in such cases, the rotation value is generally little influenced by solution, change of temperature, and substitution. In such compounds, for example, menthol and its derivatives, owing to the limited range of accessible rotation values, the rotation-dispersion cannot readily be investigated under conditions in which the characteristic diagram indicates that it would be anomalous.

At the other extreme, there are compounds of which the characteristic diagram represents lines crossing in a series of points some distance from the line of zero-rotation. In these compounds, for example, tartaric acid and its esters, the rotation is generally markedly changed by the factors of temperature, solution, and substitution; in this case, it is comparatively easy to bring the rotation to such a value that the rotation-dispersion becomes anomalous. Between these two extreme types of compounds there are, of course, intermediate types. Whilst the characteristic diagram does not represent accurately the rotation-dispersion of a compound under all conditions (see Patterson, T., 1916, 109, 1202), it nevertheless presents some advantages over previous methods of representation.

There are many facts which are difficult to explain on the hypothesis that anomalous rotation-dispersion is an indication of dynamic isomerism as postulated by Lowry and others.

Patterson (T., 1916, 109, 1204) has shown the absurdity and incompatibility of many of the hypotheses adopted in constructing formulæ to explain dynamic isomerism.

Pickard and Kenyon (T., 1915, 107, 42) have observed instances of complex rotation-dispersion with certain menthyl esters; if this is assumed to be due to the presence of dynamic isomerides, the existence of a *l*-menthyl ester having dextrorotatory power is postulated (since to produce anomalous dispersion, two substances of opposite rotatory power must be present; see Armstrong and Walker, *Trans. Faraday Soc.*, 1914, 10, 88). The great improbability of this conclusion is evident from the fact that, at present, there appears to be no record of a dextrorotatory *l*-menthyl ester.

Again, compounds of similar constitution are in the one case (*a*) anomalous at high temperatures and normal at low temperatures, and (*b*) normal at high temperatures and anomalous at low temperatures (but in each case only when the temperature-rotation curve approaches zero); dimethyl acetylchloromaleate is an example

of the first and diethyl acetylchloromalonate of the second (Walden, *Zeitsch. physikal. Chem.*, 1906, 55, 42); methyl- and hexyl- $\alpha$ -naphthylcarbinol are examples of the second case, whilst *acitetra*-hydronaphthylcarbinol belongs to the first category (Pickard and Kenyon, T., 1914, 105, 1115, 2644, 2677).

A striking confirmation of the above views is found in the results obtained by Pickard and Kenyon (T., 1915, 107, 115). The 1-naphthoate of  $\beta$ -hexyl-,  $\beta$ -heptyl-,  $\beta$ -octyl-,  $\beta$ -decyl-, and  $\beta$ -undecyl-carbinols are "simple"\* at high temperatures and "complex" at low temperatures, the 1-naphthoate of  $\gamma$ -nonyl-carbinol is "simple" at low temperatures and "complex" at high temperatures, whilst the 1-naphthoate of benzylmethylcarbinol is "simple" at all temperatures. In all these cases, if the compound exhibits "complex" rotation-dispersion, this occurs as the temperature-rotation curve approaches zero; it is particularly noteworthy that, of the above compounds, the only one that is "simple" at all temperatures has a temperature-rotation curve which never approaches zero closely.

The test for "simple" and "complex" rotation-dispersion is unfortunately not definite in cases where a compound is "simple" at one temperature and "complex" at another temperature; at intermediate temperatures, it becomes impossible definitely to classify the rotation-dispersion according to these groups. In order to illustrate this distinction between "simple" and "complex" rotation-dispersion, we have drawn a diagram (Fig. 1b) for *n*-butyl tartrate in which  $1/\alpha$  is plotted against  $\lambda^2$ . It will be seen that whilst the low-temperature lines are curved, this curvature diminishes with rise of temperature, and at 165° the line becomes almost perfectly straight. This signifies that the rotation-dispersion of *n*-butyl tartrate is "complex" at low, but almost "simple" at high, temperatures.

It should be pointed out, again, that a substance of which the rotation-dispersion can be represented by the formula

$$[\alpha] = K/\lambda^2 - \lambda_0^2,$$

within the limits of experimental error, that is, is "simple," may

\* The terms "simple" and "complex" are here used instead of normal and anomalous because the rotation can be more easily classified into simple and complex; on plotting the values for  $1/\alpha$  against  $\lambda^2$ , if a straight line results then the rotation-dispersion is simple; if a curve then the rotation-dispersion is complex. It seems advisable to retain the use of both sets of terms; thus a compound is anomalous if a maximum occurs in its rotation-dispersion curve, or is normal if no maximum is present. An anomalous compound is thus always complex, whilst a normal compound is simple or complex according to its behaviour when subjected to the above-mentioned test.



not necessarily conform to this equation with more accurate determinations of the rotation; for, as Lowry points out (*Trans. Faraday Soc.*, 1914, **10**, 57), quartz, of which the rotation-dispersion, when most accurately measured, requires three such terms, that is, is "complex," can be represented *within the same limits of accuracy as are employed in the case of optically active organic compounds* by the "simple" formula. It is, in fact, highly probable that the rotation-dispersion of optically active compounds can only be represented accurately by a series of such terms. In general, however, the constants in these terms ( $K_{(n)}$  and  $\lambda_{0(n)}$ ) are sufficiently close together for one term to suffice to express accurately enough the rotation-dispersion. When a compound, by a variation of temperature or concentration in solution, becomes "complex" in its rotation-dispersion, these constants ( $K_{(n)}$  and  $\lambda_{0(n)}$ ) (constants for the rotation-dispersion under one condition, but varying from one condition to another) have assumed such values in the several terms that these terms can no longer be united in a single term.

In the present investigation, the rotation-dispersion of *n*-butyl, *n*-heptyl, and *n*-octyl tartrates has been observed over a wide range of temperature and for a number of wave-lengths of light.

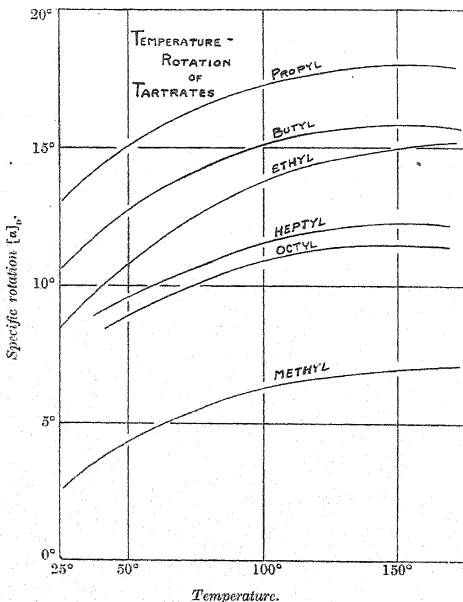
The polarimeter used was a Schmidt and Haentsch with triple field and fitted with their dispersion attachment, the illuminant being a Nernst lamp. The prism of the dispersion apparatus was calibrated by using the spectrum lines of hydrogen, mercury, and sodium; the constants of the prism for the Hartmann formula were calculated from these measurements, and hence the reading of the scale corresponding with any desired wave-length could be found. Rotations were also measured with sodium light, and these were compared with the readings obtained with the dispersion apparatus when the scale was set at the point corresponding with the mean of the sodium lines; in all cases, these readings were equal within the limits of experimental error.

The experimental error is much greater in the violet and extreme red than in the middle part of the spectrum, owing to the difficulty in measurement and also to the reduction in luminosity.

The rotation-dispersion of methyl, ethyl, and propyl tartrates has already been investigated for a wide range of temperatures by Winther and Walden. Winther (*Zeitsch. physikal. Chem.*, 1902, **41**, 161) has recorded observations from about 20° to 100°, whilst Walden (*Ber.*, 1905, **38**, 366) measured rotations from -65° to 170°. We have investigated the rotation-dispersion of butyl tartrate from 9° to 170°, and of heptyl and octyl tartrates from their melting points up to about 170°; it was found that the com-

pounds decomposed slightly at the higher temperatures, but by again taking readings at a lower temperature, it was shown that no appreciable change in the rotation had occurred. The readings of both Winther and Walden were taken with coloured lights obtained by means of light filters; more recently, Lowry and others have determined the rotation-dispersion of methyl and ethyl

FIG. 1.



tartrates at two or three temperatures for different wave-lengths of light obtained from the mercury and cadmium arcs (T., 1915, 107, 1173, 1187). The temperature-rotation curves of all these esters exhibit maxima, and for comparison, in Fig. 1, the temperature-rotation curves for sodium light for butyl, heptyl, and octyl tartrates are given, together with those obtained by Patterson (T.,

1904, 85, 765; 1913, 103, 173) for methyl, ethyl, and propyl tartrates.

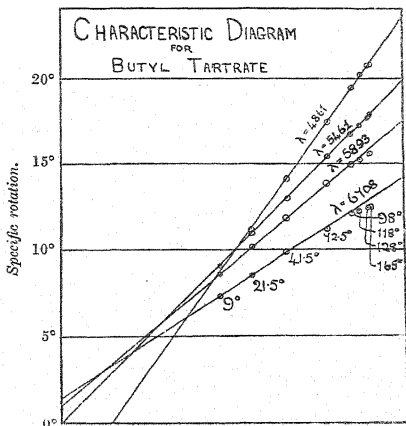
In the following table, the temperatures at which a maximum observed rotation for different wave-lengths is obtained, are recorded for the several members of the series.

TABLE I.

*Maxima in Observed Rotation.*

	$\lambda =$	Red.	Yellow.	Green.	Blue.	Violet.
Methyl tartrate .....	665	160°	—	180°	—	—
Ethyl     " .....	140	150°	155	170°	180°	—
Propyl   " .....	115	120	125	125	134	—
Butyl     " .....	120	125	130	135	—	—
Heptyl   " .....	125	130	135	140	—	—
Octyl     " .....	125	130	135	140	—	—

FIG. 1A.



The values for the first three members of the series are taken from Walden (*loc. cit.*) and from Patterson (T., 1913, 103, 149, 165).

In the temperature-rotation curves for butyl, heptyl, and octyl tartrates (Figs. 2, 3, and 4 respectively), the maxima in the

specific rotation for all wave-lengths lie at temperatures above  $150^{\circ}$ .

The rotation-dispersion curves for butyl, heptyl, and octyl tartrates (Figs. 5, 6, and 7 respectively) exhibit a maximum rotation at the lower temperatures only.

The following figures show the effect of ascending the series on the rotation of the tartrates.

FIG. 1b.

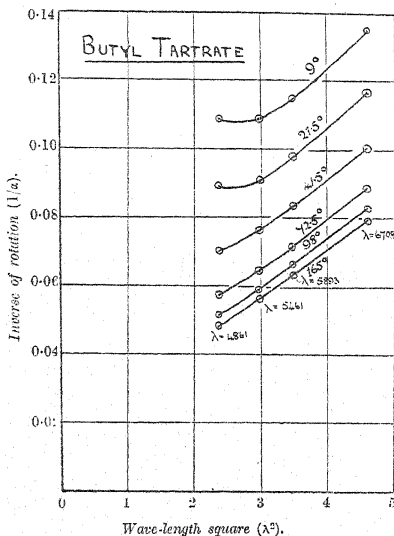


TABLE II.

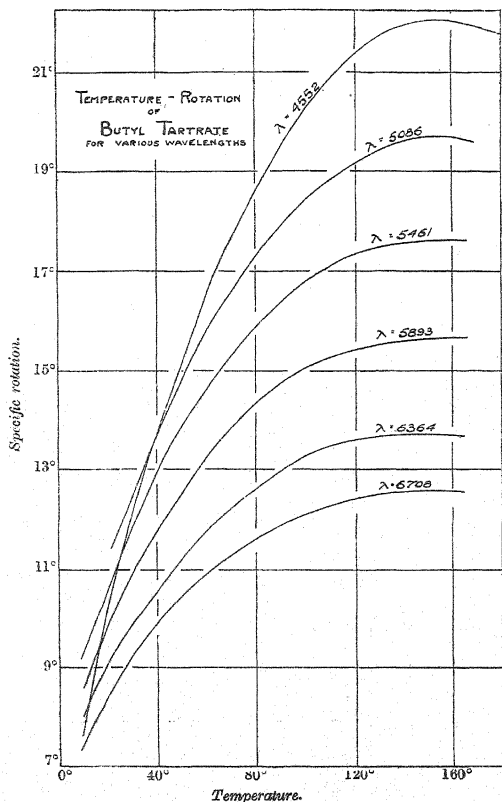
	Methyl.*	Ethyl.*	Propyl.*	Butyl.	Heptyl.	Octyl.
$\alpha_D^{100}$ .....	7.73°	15.30°	18.25°	15.40°	10.88°	10.16°
$[\alpha]_D^{100}$ .....	6.18	13.70	17.20	15.00	11.44	10.84
$[M]_D^{100}$ .....	11.00	28.21	40.10	39.34	39.57	39.55

\* Patterson (*loc. cit.*).

Thus in the observed and specific rotations there is a maximum at the propyl member of the series; but in the molecular rotation

the curve for the series increases until the propyl member is reached, after which it remains practically constant at about the

FIG. 2.

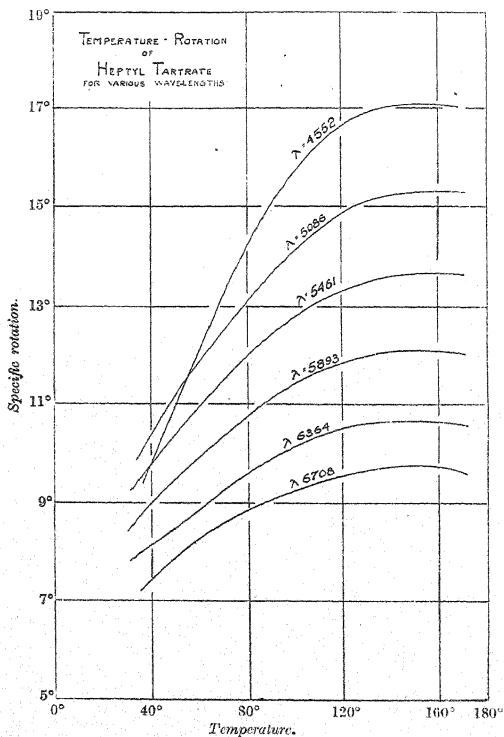


value  $39.5^\circ$ . It will be noticed that the maxima in the temperature-observed-rotation figures for the series (see table I) are

reached at the *lowest* temperature in the case of the propyl member.

By reference to Fig. 1, it is seen that the temperature-rotation

FIG. 3.

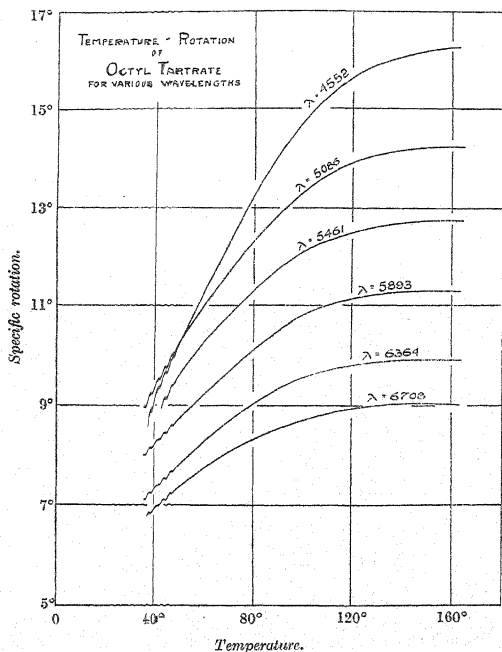


curves for sodium light for propyl, butyl, heptyl, and octyl tartrates are approximately parallel, therefore the maximum in the specific rotation occurs at about the same temperature for all these tartrates.

In Fig. 8, the molecular rotations for various coloured lights are shown for the several members of the series for a temperature of  $100^{\circ}$ ; the molecular rotation for all colours remains approximately constant after the propyl member is reached.

Butyl, heptyl, and octyl tartrates are "anomalous" at low

FIG. 4.



temperatures, and tend to become "normal" at high temperatures; this is readily seen by reference to Figs. 2, 3, and 4, in which the curves for the shorter wave-lengths cross the curves for the longer wave-lengths at low temperatures; the ratio, therefore, of any rotation for any wave-length to that for mercury-green

( $\lambda=5461$ ) varies considerably at low temperatures. At higher temperatures, the figures in the following table show that the ratio tends to become constant.

FIG. 5.

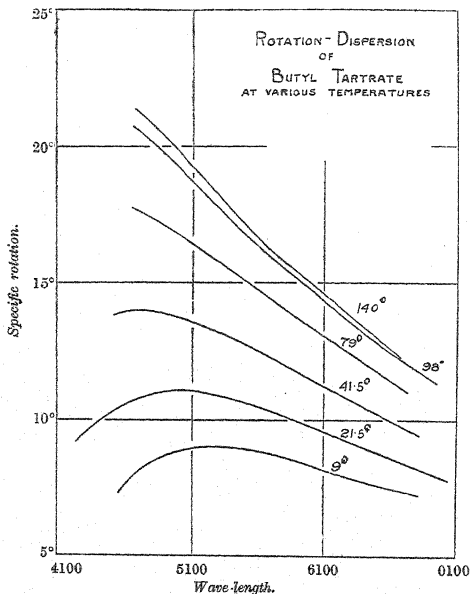


TABLE III.

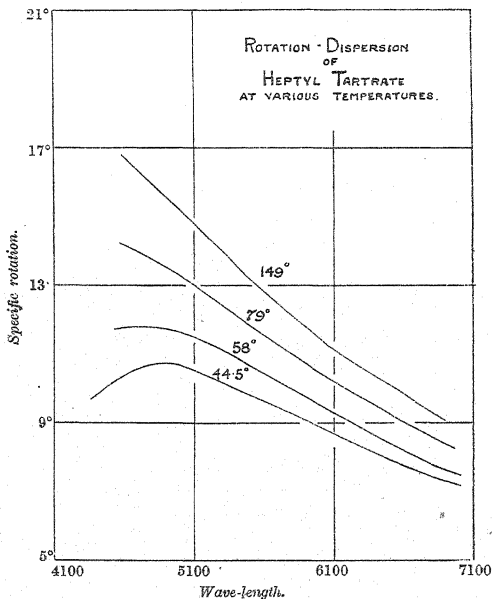
	$\lambda =$			(Mercury Green.)	
Butyl tartrate at 21.5°	6708	5893	5461	5086	
" " 41.5	0.773	0.928	1.0	1.028	
" " 98	0.758	0.911	1.0	1.070	
" " 128	0.723	0.892	1.0	1.098	
" " 165	0.707	0.888	1.0	1.119	
" " 165	0.709	0.888	1.0	1.113	
Heptyl tartrate at 168°	0.707	0.886	1.0	1.116	
Octyl tartrate at 165°	0.707	0.886	1.0	1.114	

The ratios for butyl, heptyl, and octyl tartrates for the same wave-lengths are approximately equal at the higher temperatures;



whilst these ratios are rather high, they are not sufficiently high to indicate that the esters are abnormal in their rotation-dispersion. On applying the test for "simple" and "complex" rotatory dispersion (see footnote, p. 640), however, it is found that at all temperatures the rotation-dispersion is complex, but the farther the rotation is removed from the zero line by raising the tempera-

FIG. 6.



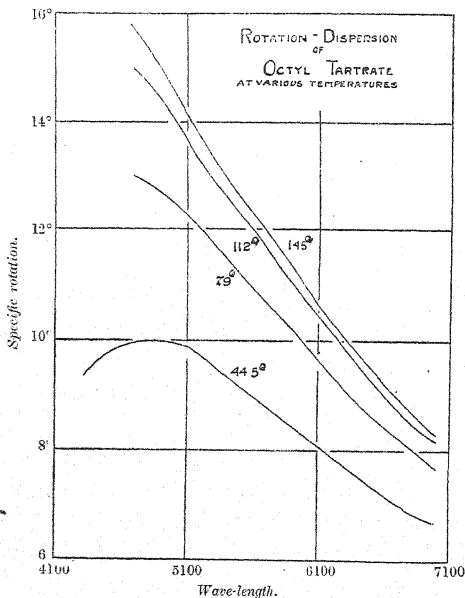
ture, the more simple (or less complex) does the rotation become; thus at high temperatures the curve  $1/\alpha$  against  $\lambda^2$  has only a very slight curvature, for example, see Fig. 1B.

#### EXPERIMENTAL.

The esters were prepared by a modification of the usual hydrochloric acid method of esterification; four molecular proportions of alcohol and one of acid were mixed and saturated with dry

hydrogen chloride while the mixture was heated on a water-bath. After leaving the mixture for a few weeks, it was again saturated with hydrogen chloride, this time in the cold; the hydrochloric acid, water, and excess of alcohol were distilled off, and the residual ester was then distilled in a partial vacuum of 12 mm. (in the case of heptyl and octyl tartrates, recrystallisation from light petroleum

FIG. 7.



was also adopted for the purification of the residual ester). By this method of esterification, an almost theoretical yield of ester (calculated on the acid used) was obtained.

In the case of heptyl tartrate, specimens were also prepared in the following ways:

(1) The mixture of acid and alcohol was saturated with hydrogen chloride in the cold, the hydrochloric acid being removed, after

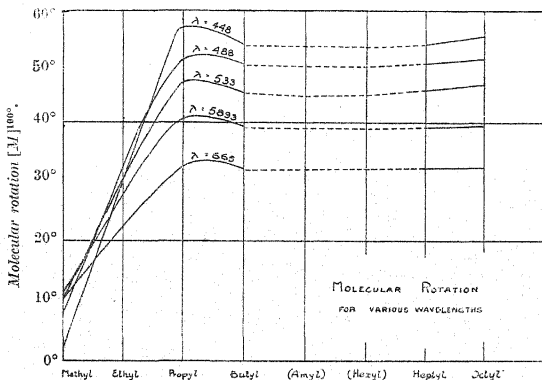
several weeks, by keeping in a desiccator; the ester crystallised out, and was recrystallised from light petroleum.

The heptyl tartrate obtained in this way had  $\alpha_D^{100}$   $10.90^\circ$ .

(2) Patterson and Dickinson's method (T., 1901, **79**, 280) was employed, commencing with ethyl tartrate. The product had  $\alpha_D^{100}$   $10.85^\circ$ .

The heptyl tartrate prepared by the method given above had  $\alpha_D^{100}$   $10.88^\circ$ , and thus no appreciable racemisation is produced by this method of esterification.

FIG. 8.



*n*-Butyl tartrate was prepared from butyl alcohol boiling at  $116.5\text{--}117^\circ/752$  mm. (The boiling point of pure *n*-butyl alcohol is  $116.5\text{--}117.2^\circ/760$  mm.) After six distillations in a vacuum of 12 mm., the butyl tartrate had  $\alpha_D^{25}$   $22.25^\circ$  ( $l=2$ -dcm.); this rotation is slightly less than that recorded by Freundler (*Ann. Chim. Phys.*, 1893, [vii], **3**, 446), namely,  $\alpha_D^{25}$   $22.51^\circ$  ( $l=2$ -dcm.). A specimen of butyl tartrate prepared from a slightly impure alcohol (b. p.  $115\text{--}117^\circ$ ), however, we found to have  $\alpha_D^{25}$   $24.64^\circ$  ( $l=2$ -dcm.). Butyl tartrate melts at  $22^\circ$  (Freundler, *Bull. Soc. chim.*, 1894, [iii], **11**, 309, gives  $21\text{--}22^\circ$ ) and boils at  $178^\circ/12$  mm. (Freundler gives  $208^\circ/12$  mm.). It exhibits a maximum in its rotation-dispersion within the wave-lengths recorded at temperatures below  $70^\circ$ .

#### Densities.

Temperature	$18^\circ$	$61.0^\circ$	$101.2^\circ$	$132.5^\circ$	$169.5^\circ$
$D_4^{25}$ .....	1.0968	1.0600	1.0246	0.9986	0.9654

## BUTYL TARTRATE.

*Temperature 9°. Density 1.1044.*

$\lambda$ .....	6708	6563	6147	5893	5769	5570	5461	5219	4861	4662
$\alpha$ ( $l=2$ -decim.) .....	16.44	16.96	18.39	19.16	19.48	19.71	20.18	20.47	19.4	17.9
$[\alpha]$ .....	7.44	7.68	8.32	8.67	8.82	8.92	9.13	9.26	8.7	8.1
$[M]$ .....	19.5	20.14	21.85	22.76	23.14	23.41	23.97	24.31	23.1	21.3

*Temperature 21.5°. Density 1.0934.*

$\lambda$ .....	6923	6708	6563	6364	6147	6025	5893	5769	5679	5568
$\alpha$ ( $l=2$ -decim.) .....	17.8	18.69	19.24	20.08	21.05	21.63	22.25	22.80	23.15	23.66
$[\alpha]$ .....	8.1	8.55	8.80	9.18	9.63	9.91	10.20	10.45	10.61	10.81
$[M]$ .....	21.4	22.43	23.09	24.09	25.26	26.01	26.75	27.41	27.84	28.38
$\lambda$ .....	5461	5323	5219	5154	5086	5004	4925	4861	4692	4552
$\alpha$ ( $l=2$ -decim.) .....	24.00	24.39	24.54	24.59	24.66	24.61	24.56	24.50	24.0	23.4
$[\alpha]$ .....	11.00	11.18	11.25	11.27	11.30	11.28	11.26	11.23	11.0	10.7
$[M]$ .....	28.86	29.33	29.51	29.57	29.65	29.69	29.53	29.46	28.8	28.2

*Temperature 41.5°. Density 1.0759.*

$\lambda$ .....	6708	6563	6364	6147	6025	5893	5769	5679	5461	5323
$\alpha$ ( $l=2$ -decim.) .....	21.36	22.00	23.11	24.26	24.94	25.66	26.39	26.89	28.14	28.71
$[\alpha]$ .....	9.93	10.22	10.74	11.27	11.59	11.92	12.27	12.50	13.08	13.34
$[M]$ .....	26.04	26.83	28.18	29.58	30.41	31.29	32.18	32.79	34.31	35.01
$\lambda$ .....	5323	5219	5105	5086	5004	4861	4785	4662	4552	4411
$\alpha$ ( $l=2$ -decim.) .....	28.71	29.28	29.83	30.10	30.22	30.54	30.6	30.5	30.4	30.1
$[\alpha]$ .....	13.34	13.61	13.86	13.99	14.04	14.19	14.2	14.1	14.1	14.1
$[M]$ .....	35.01	35.70	36.38	36.70	36.85	37.2	37.3	37.2	37.1	37.1

*Temperature 72.5°. Density 1.0492.*

$\lambda$ .....	6563	6364	6147	6025	5893	5769
$\alpha$ ( $l=2$ -dem.) .....	24.61	25.93	27.41	28.29	29.18	30.13
$[\alpha]$ .....	11.73	12.36	13.06	13.48	13.91	14.36
$[\eta]$ .....	30.77	32.42	34.27	35.37	36.49	37.69
$\lambda$ .....	5568	5461	5219	5086	4861	4662
$\alpha$ ( $l=2$ -dem.) .....	31.58	32.41	34.12	35.09	36.6	37.6
$[\alpha]$ .....	15.05	15.44	16.26	16.72	17.4	17.9
$[\eta]$ .....	39.49	40.51	42.67	43.88	45.8	47.0

*Temperature 98°. Density 1.0269.*

$\lambda$ .....	6708	6563	6364	6147	6025	5893	5769
$\alpha$ ( $l=2$ -dem.) .....	24.88	25.76	27.15	28.74	29.70	30.71	31.72
$[\alpha]$ .....	12.11	12.54	13.22	13.99	14.46	14.95	15.45
$[\eta]$ .....	31.79	32.91	34.69	36.72	37.95	39.23	40.62
$\lambda$ .....	5461	5219	5086	4861	4662	4552	4359
$\alpha$ ( $l=2$ -dem.) .....	34.40	36.71	37.80	39.90	41.4	41.8	41.6
$[\alpha]$ .....	16.75	17.87	18.40	19.43	20.2	20.3	20.2
$[\eta]$ .....	43.90	46.90	48.29	50.98	52.9	53.4	53.1

*Temperature 118°. Density 1.0099.*

$\lambda$ .....	6708	6563	6364	6147	6025	5893	5769
$\alpha$ ( $l=2$ -dem.) .....	25.02	25.91	27.32	29.00	29.94	31.01	32.10
$[\alpha]$ .....	12.39	12.83	13.63	14.36	14.82	15.35	15.89
$[\eta]$ .....	32.50	33.66	35.49	37.68	38.90	40.29	41.70
$\lambda$ .....	5461	5323	5219	5154	5086	4861	4662
$\alpha$ ( $l=2$ -dem.) .....	34.87	36.29	37.14	37.79	38.44	40.82	42.3
$[\alpha]$ .....	17.26	17.97	18.39	18.71	19.03	20.21	20.9
$[\eta]$ .....	45.31	47.14	48.25	49.10	49.94	53.03	54.9

*Temperature 128°. Density 1.0011.*

$\lambda$ .....	6768	6563	6364	6147	6025	5893	5769
$\alpha$ ( $l=1$ -dem.) .....	12.4	12.92	13.64	14.53	14.97	15.55	16.10
$[\alpha]$ .....	12.4	12.91	13.63	14.51	14.95	15.53	16.08
$[\text{M}]$ .....	32.5	33.86	35.75	38.09	39.24	40.76	42.20
$\lambda$ .....	5679	5568	5401	5219	5086	4861	4785
$\alpha$ ( $l=1$ -dem.) .....	16.48	16.99	17.55	18.67	19.3	20.4	21.0
$[\alpha]$ .....	16.46	16.97	17.53	18.65	19.5	20.4	21.0
$[\text{M}]$ .....	43.20	44.53	46.0	48.92	51.2	53.5	55.0

*Temperature 140°. Density 0.9906.*

$\lambda$ .....	6708	6563	6364	6147	6025	5893	5769	5679	5568
$\alpha$ ( $l=2$ -dem.) .....	24.65	25.77	27.09	28.82	29.86	31.00	32.15	32.92	33.97
$[\alpha]$ .....	12.44	13.00	13.67	14.54	15.08	15.65	16.23	16.62	17.15
$[\text{M}]$ .....	32.65	34.13	35.88	38.16	39.56	41.06	42.58	43.60	44.99
$\lambda$ .....	5461	5323	5219	5154	5086	4861	4662	4552	
$\alpha$ ( $l=2$ -dem.) .....	34.92	36.42	37.41	38.01	38.88	41.14	42.3	43.6	
$[\alpha]$ .....	17.63	18.38	18.88	19.18	19.62	20.76	21.4	22.0	
$[\text{M}]$ .....	46.25	48.24	49.55	50.34	51.50	54.49	56.3	57.7	

Temperature 151°. Density 0.981.		
$\lambda$ .....	6708	6563
$\alpha$ ( $l=1$ -dem.) .....	12.30	12.72
$[\alpha]$ .....	12.54	12.97
$[\eta]$ .....	32.90	34.02
$\lambda$ .....	5461	5323
$\alpha$ ( $l=1$ -dem.) ..	17.30	17.90
$[\alpha]$ .....	17.66	18.24
$[\eta]$ .....	46.32	47.88
	6147	6025
	6364	6219
	13.42	13.88
	14.26	14.73
	15.39	15.88
	16.19	16.57
	18.19	18.72
	22.1	22.7
	22.6	23.1
	22.7	23.4
	22.8	23.6
	22.9	23.8
	23.0	24.0
	23.1	24.2
	23.2	24.4
	23.3	24.6
	23.4	24.8
	23.5	25.0
	23.6	25.2
	23.7	25.4
	23.8	25.6
	23.9	25.8
	24.0	26.0
	24.1	26.2
	24.2	26.4
	24.3	26.6
	24.4	26.8
	24.5	27.0
	24.6	27.2
	24.7	27.4
	24.8	27.6
	24.9	27.8
	25.0	28.0
	25.1	28.2
	25.2	28.4
	25.3	28.6
	25.4	28.8
	25.5	29.0
	25.6	29.2
	25.7	29.4
	25.8	29.6
	25.9	29.8
	26.0	30.0
	26.1	30.2
	26.2	30.4
	26.3	30.6
	26.4	30.8
	26.5	31.0
	26.6	31.2
	26.7	31.4
	26.8	31.6
	26.9	31.8
	27.0	32.0
	27.1	32.2
	27.2	32.4
	27.3	32.6
	27.4	32.8
	27.5	33.0
	27.6	33.2
	27.7	33.4
	27.8	33.6
	27.9	33.8
	28.0	34.0
	28.1	34.2
	28.2	34.4
	28.3	34.6
	28.4	34.8
	28.5	35.0
	28.6	35.2
	28.7	35.4
	28.8	35.6
	28.9	35.8
	29.0	36.0
	29.1	36.2
	29.2	36.4
	29.3	36.6
	29.4	36.8
	29.5	37.0
	29.6	37.2
	29.7	37.4
	29.8	37.6
	29.9	37.8
	30.0	38.0
	30.1	38.2
	30.2	38.4
	30.3	38.6
	30.4	38.8
	30.5	39.0
	30.6	39.2
	30.7	39.4
	30.8	39.6
	30.9	39.8
	31.0	40.0
	31.1	40.2
	31.2	40.4
	31.3	40.6
	31.4	40.8
	31.5	41.0
	31.6	41.2
	31.7	41.4
	31.8	41.6
	31.9	41.8
	32.0	42.0
	32.1	42.2
	32.2	42.4
	32.3	42.6
	32.4	42.8
	32.5	43.0
	32.6	43.2
	32.7	43.4
	32.8	43.6
	32.9	43.8
	33.0	44.0
	33.1	44.2
	33.2	44.4
	33.3	44.6
	33.4	44.8
	33.5	45.0
	33.6	45.2
	33.7	45.4
	33.8	45.6
	33.9	45.8
	34.0	46.0
	34.1	46.2
	34.2	46.4
	34.3	46.6
	34.4	46.8
	34.5	47.0
	34.6	47.2
	34.7	47.4
	34.8	47.6
	34.9	47.8
	35.0	48.0
	35.1	48.2
	35.2	48.4
	35.3	48.6
	35.4	48.8
	35.5	49.0
	35.6	49.2
	35.7	49.4
	35.8	49.6
	35.9	49.8
	36.0	50.0
	36.1	50.2
	36.2	50.4
	36.3	50.6
	36.4	50.8
	36.5	51.0
	36.6	51.2
	36.7	51.4
	36.8	51.6
	36.9	51.8
	37.0	52.0
	37.1	52.2
	37.2	52.4
	37.3	52.6
	37.4	52.8
	37.5	53.0
	37.6	53.2
	37.7	53.4
	37.8	53.6
	37.9	53.8
	38.0	54.0
	38.1	54.2
	38.2	54.4
	38.3	54.6
	38.4	54.8
	38.5	55.0
	38.6	55.2
	38.7	55.4
	38.8	55.6
	38.9	55.8
	39.0	56.0
	39.1	56.2
	39.2	56.4
	39.3	56.6
	39.4	56.8
	39.5	57.0
	39.6	57.2
	39.7	57.4
	39.8	57.6
	39.9	57.8
	40.0	58.0
	40.1	58.2
	40.2	58.4
	40.3	58.6
	40.4	58.8
	40.5	59.0
	40.6	59.2
	40.7	59.4
	40.8	59.6
	40.9	59.8
	41.0	60.0
	41.1	60.2
	41.2	60.4
	41.3	60.6
	41.4	60.8
	41.5	61.0
	41.6	61.2
	41.7	61.4
	41.8	61.6
	41.9	61.8
	42.0	62.0
	42.1	62.2
	42.2	62.4
	42.3	62.6
	42.4	62.8
	42.5	63.0
	42.6	63.2
	42.7	63.4
	42.8	63.6
	42.9	63.8
	43.0	64.0
	43.1	64.2
	43.2	64.4
	43.3	64.6
	43.4	64.8
	43.5	65.0
	43.6	65.2
	43.7	65.4
	43.8	65.6
	43.9	65.8
	44.0	66.0
	44.1	66.2
	44.2	66.4
	44.3	66.6
	44.4	66.8
	44.5	67.0
	44.6	67.2
	44.7	67.4
	44.8	67.6
	44.9	67.8
	45.0	68.0
	45.1	68.2
	45.2	68.4
	45.3	68.6
	45.4	68.8
	45.5	69.0
	45.6	69.2
	45.7	69.4
	45.8	69.6
	45.9	69.8
	46.0	70.0
	46.1	70.2
	46.2	70.4
	46.3	70.6
	46.4	70.8
	46.5	71.0
	46.6	71.2
	46.7	71.4
	46.8	71.6
	46.9	71.8
	47.0	72.0
	47.1	72.2
	47.2	72.4
	47.3	72.6
	47.4	72.8
	47.5	73.0
	47.6	73.2
	47.7	73.4
	47.8	73.6
	47.9	73.8
	48.0	74.0
	48.1	74.2
	48.2	74.4
	48.3	74.6
	48.4	74.8
	48.5	75.0
	48.6	75.2
	48.7	75.4
	48.8	75.6
	48.9	75.8
	49.0	76.0
	49.1	76.2
	49.2	76.4
	49.3	76.6
	49.4	76.8
	49.5	77.0
	49.6	77.2
	49.7	77.4
	49.8	77.6
	49.9	77.8
	50.0	78.0
	50.1	78.2
	50.2	78.4
	50.3	78.6
	50.4	78.8
	50.5	79.0
	50.6	79.2
	50.7	79.4
	50.8	79.6
	50.9	79.8
	51.0	80.0
	51.1	80.2
	51.2	80.4
	51.3	80.6
	51.4	80.8
	51.5	81.0
	51.6	81.2
	51.7	81.4
	51.8	81.6
	51.9	81.8
	52.0	82.0
	52.1	82.2
	52.2	82.4
	52.3	82.6
	52.4	82.8
	52.5	83.0
	52.6	83.2
	52.7	83.4
	52.8	83.6
	52.9	83.8
	53.0	84.0
	53.1	84.2
	53.2	84.4
	53.3	84.6
	53.4	84.8
	53.5	85.0
	53.6	85.2
	53.7	85.4
	53.8	85.6
	53.9	85.8
	54.0	86.0
	54.1	86.2
	54.2	86.4
	54.3	86.6
	54.4	86.8
	54.5	87.0
	54.6	87.2
	54.7	87.4
	54.8	87.6
	54.9	87.8
	55.0	88.0
	55.1	88.2
	55.2	88.4
	55.3	88.6
	55.4	88.8
	55.5	89.0
	55.6	89.2
	55.7	89.4
	55.8	89.6
	55.9	89.8
	56.0	90.0
	56.1	90.2
	56.2	90.4
	56.3	90.6
	56.4	90.8
	56.5	91.0
	56.6	91.2
	56.7	91.4
	56.8	91.6
	56.9	91.8
	57.0	92.0
	57.1	92.2
	57.2	92.4
	57.3	92.6
	57.4	92.8
	57.5	93.0
	57.6	93.2
	57.7	93.4
	57.8	93.6
	57.9	93.8
	58.0	94.0
	58.1	94.2
	58.2	94.4
	58.3	94.6
	58.4	94.8
	58.5	95.0
	58.6	95.2
	58.7	95.4
	58.8	95.6
	58.9	95.8
	59.0	96.0
	59.1	96.2
	59.2	96.4
	59.3	96.6
	59.4	96.8
	59.5	97.0
	59.6	97.2
	59.7	97.4
	59.8	97.6
	59.9	97.8
	60.0	98.0
	60.1	98.2
	60.2	98.4
	60.3	98.6
	60.4	98.8
	60.5	99.0
	60.6	99.2
	60.7	99.4
	60.8	99.6
	60.9	99.8
	61.0	100.0

Temperature 165°. Density 0.969.									
$\lambda$ .....	6708	6563	6364	6147	6025	5893	5769	5679	5568
$\alpha$ ( $l=1$ -dem.) .....	12.13	12.59	13.30	14.14	14.59	15.20	15.74	16.15	16.63
$[\alpha]$ .....	12.52	12.99	13.72	14.58	15.06	15.69	16.25	16.67	17.16
$[\eta]$ .....	32.85	34.10	36.02	38.27	39.51	41.16	42.63	43.74	45.04
$\lambda$ .....	5461	5323	5219	5086	4861	4662	4552	4454	
$\alpha$ ( $l=1$ -dem.) .....	17.12	17.85	18.38	19.05	19.96	21.2	21.6	22.4	
$[\alpha]$ .....	17.67	18.42	18.97	19.66	20.60	21.9	22.3	23.1	
$[\eta]$ .....	46.36	48.34	49.78	51.59	54.05	57.4	58.6	60.7	

## HEPTYL TARTRATE.

Temperature 44.5°. Density 0.9952.

$\lambda$ .....	6708	6563	6364	6147	6025	5893	5769	5679	5568
$\alpha$ ( $l=2$ -dem.) .....	15.25	15.76	16.53	17.31	17.80	18.26	18.77	19.18	19.58
$[\alpha]$ .....	7.66	7.92	8.30	8.70	8.94	9.17	9.43	9.64	9.84
$[\eta]$ .....	26.56	27.44	28.79	30.14	31.00	31.79	32.68	33.40	34.10
$\lambda$ .....	5461	5323	5219	5154	5086	5004	4861	4662	4454
$\alpha$ ( $l=2$ -dem.) .....	19.97	20.43	20.78	21.02	21.14	21.3	21.45	21.0	20.1
$[\alpha]$ .....	10.03	10.27	10.44	10.56	10.62	10.70	10.77	10.6	10.1
$[\eta]$ .....	34.78	35.58	36.19	36.60	36.81	37.1	37.35	36.6	35.0

Temperature 58°. Density 0.9848.

$\lambda$ .....	6708	6563	6364	6147	6025	5893	5769	5679	5568
$\alpha$ ( $l=1$ -dem.) .....	8.06	8.31	8.70	9.15	9.37	9.70	10.01	10.23	10.46
$[\alpha]$ .....	8.18	8.44	8.83	9.29	9.51	9.85	10.17	10.39	10.62
$[\eta]$ .....	28.36	29.24	30.62	32.20	32.98	34.14	35.23	36.01	36.82
$\lambda$ .....	5461	5323	5219	5154	5086	5004	4861	4662	4454
$\alpha$ ( $l=1$ -dem.) .....	10.70	10.96	11.20	11.33	11.46	11.60	11.70	11.7	11.5
$[\alpha]$ .....	10.86	11.12	11.37	11.50	11.64	11.78	11.88	11.9	11.7
$[\eta]$ .....	37.66	38.54	39.42	39.88	40.33	40.83	41.18	41.3	40.6

Temperature 79°. Density 0.9685.

$\lambda$ .....	6708	6563	6364	6147	6025	5893	5769	5679	5568
$\alpha$ ( $l=2$ -dem.) .....	17.19	17.83	18.69	19.67	20.36	21.07	21.74	22.26	22.82
$[\alpha]$ .....	8.87	9.20	9.65	10.16	10.51	10.88	11.23	11.49	11.78
$[\eta]$ .....	30.76	31.90	33.44	35.20	36.43	37.70	38.90	39.83	40.84
$\lambda$ .....	5461	5323	5219	5154	5086	5004	4861	4662	4454
$\alpha$ ( $l=2$ -dem.) .....	23.39	24.19	24.65	25.16	25.52	25.90	26.51	27.3	27.8
$[\alpha]$ .....	12.08	12.49	12.78	12.99	13.18	13.37	13.69	14.1	14.1
$[\eta]$ .....	41.85	42.29	44.11	45.02	45.69	46.35	47.44	48.85	49.4



		<i>Temperature 100°.</i>		<i>Density 0.9520.</i>	
$\lambda$ .....	6708	6563	6364	6147	5893
$\alpha$ ( $l=2$ -dem.) .....	17.66	18.27	19.32	20.40	21.02
$[\alpha]$ .....	9.27	9.59	10.15	10.71	11.04
$[\eta]$ .....	32.15	33.26	35.17	37.14	38.26
$\lambda$ .....	5461	5323	5219	5154	5086
$\alpha$ ( $l=2$ -dem.) .....	24.34	25.24	26.80	28.35	29.74
$[\alpha]$ .....	12.79	13.26	13.60	13.84	14.04
$[\eta]$ .....	44.31	45.95	47.15	47.97	48.68

		<i>Temperature 110°.</i>		<i>Density 0.9442.</i>	
$\lambda$ .....	6708	6563	6364	6147	5893
$\alpha$ ( $l=2$ -dem.) .....	17.92	18.59	19.53	20.66	21.34
$[\alpha]$ .....	9.49	9.84	10.34	10.94	11.30
$[\eta]$ .....	32.89	34.12	35.85	37.92	39.17
$\lambda$ .....	5461	5323	5219	5154	5086
$\alpha$ ( $l=2$ -dem.) .....	24.82	25.78	26.74	27.15	27.58
$[\alpha]$ .....	13.14	13.65	14.16	14.38	14.60
$[\eta]$ .....	45.56	47.32	49.08	49.83	50.62

		<i>Temperature 125°.</i>		<i>Density 0.9328.</i>	
$\lambda$ .....	6708	6563	6364	6147	5893
$\alpha$ ( $l=2$ -dem.) .....	18.03	18.66	19.66	20.82	21.54
$[\alpha]$ .....	9.66	10.00	10.54	11.16	11.55
$[\eta]$ .....	33.50	34.68	36.52	38.68	40.02
$\lambda$ .....	5508	5461	5219	5154	5086
$\alpha$ ( $l=2$ -dem.) .....	24.42	25.15	26.98	27.66	28.04
$[\alpha]$ .....	13.09	13.48	14.46	14.83	15.03
$[\eta]$ .....	45.37	46.72	50.12	51.39	52.09

5679	5679	5679	5679	5679	5679
23.07	23.07	23.07	23.07	23.07	23.07
12.12	12.12	12.12	12.12	12.12	12.12
42.0	42.0	42.0	42.0	42.0	42.0

5769	5769	5769	5769	5769	5769
22.48	22.48	22.48	22.48	22.48	22.48
11.81	11.81	11.81	11.81	11.81	11.81
40.92	40.92	40.92	40.92	40.92	40.92

5893	5893	5893	5893	5893	5893
21.76	21.76	21.76	21.76	21.76	21.76
11.43	11.43	11.43	11.43	11.43	11.43
39.61	39.61	39.61	39.61	39.61	39.61

6025	6025	6025	6025	6025	6025
21.02	21.02	21.02	21.02	21.02	21.02
11.04	11.04	11.04	11.04	11.04	11.04
38.26	38.26	38.26	38.26	38.26	38.26

5004	5004	5004	5004	5004	5004
27.24	27.24	27.24	27.24	27.24	27.24
14.31	14.31	14.31	14.31	14.31	14.31
49.6	49.6	49.6	49.6	49.6	49.6

5086	5086	5086	5086	5086	5086
26.74	26.74	26.74	26.74	26.74	26.74
14.04	14.04	14.04	14.04	14.04	14.04
48.68	48.68	48.68	48.68	48.68	48.68

5154	5154	5154	5154	5154	5154
26.35	26.35	26.35	26.35	26.35	26.35
13.84	13.84	13.84	13.84	13.84	13.84
47.97	47.97	47.97	47.97	47.97	47.97

5154	5154	5154	5154	5154	5154
26.35	26.35	26.35	26.35	26.35	26.35
13.84	13.84	13.84	13.84	13.84	13.84
47.97	47.97	47.97	47.97	47.97	47.97

5004	5004	5004	5004	5004	5004
27.24	27.24	27.24	27.24	27.24	27.24
14.31	14.31	14.31	14.31	14.31	14.31
49.6	49.6	49.6	49.6	49.6	49.6

5086	5086	5086	5086	5086	5086
26.74	26.74	26.74	26.74	26.74	26.74
14.04	14.04	14.04	14.04	14.04	14.04
48.68	48.68	48.68	48.68	48.68	48.68

5679	5679	5679	5679	5679	5679
23.40	23.40	23.40	23.40	23.40	23.40
12.39	12.39	12.39	12.39	12.39	12.39
42.95	42.95	42.95	42.95	42.95	42.95

5769	5769	5769	5769	5769	5769
22.88	22.88	22.88	22.88	22.88	22.88
12.11	12.11	12.11	12.11	12.11	12.11
41.96	41.96	41.96	41.96	41.96	41.96

5893	5893	5893	5893	5893	5893
22.14	22.14	22.14	22.14	22.14	22.14
11.72	11.72	11.72	11.72	11.72	11.72
40.64	40.64	40.64	40.64	40.64	40.64

6025	6025	6025	6025	6025	6025
21.34	21.34	21.34	21.34	21.34	21.34
11.30	11.30	11.30	11.30	11.30	11.30
39.17	39.17	39.17	39.17	39.17	39.17

5004	5004	5004	5004	5004	5004
28.20	28.20	28.20	28.20	28.20	28.20
14.93	14.93	14.93	14.93	14.93	14.93
51.76	51.76	51.76	51.76	51.76	51.76

5086	5086	5086	5086	5086	5086
27.58	27.58	27.58	27.58	27.58	27.58
14.60	14.60	14.60	14.60	14.60	14.60
50.62	50.62	50.62	50.62	50.62	50.62

5154	5154	5154	5154	5154	5154
27.15	27.15	27.15	27.15	27.15	27.15
14.38	14.38	14.38	14.38	14.38	14.38
49.83	49.83	49.83	49.83	49.83	49.83

5461	5461	5461	5461	5461	5461
24.82	24.82	24.82	24.82	24.82	24.82
13.14	13.14	13.14	13.14	13.14	13.14
45.56	45.56	45.56	45.56	45.56	45.56

5461	5461	5461	5461	5461	5461
24.82	24.82	24.82	24.82	24.82	24.82
13.14	13.14	13.14	13.14	13.14	13.14
45.56	45.56	45.56	45.56	45.56	45.56

5461	5461	5461	5461	5461	5461
24.82	24.82	24.82	24.82	24.82	24.82
13.14	13.14	13.14	13.14	13.14	13.14
45.56	45.56	45.56	45.56	45.56	45.56

4662	4662	4662	4662	4662	4662
31.2	31.2	31.2	31.2	31.2	31.2
16.1	16.1	16.1	16.1	16.1	16.1
55.9	55.9	55.9	55.9	55.9	55.9

4861	4861	4861	4861	4861	4861
28.77	28.77	28.77	28.77	28.77	28.77
15.24	15.24	15.24	15.24	15.24	15.24
52.8	52.8	52.8	52.8	52.8	52.8

4861	4861	4861	4861	4861	4861
28.77	28.77	28.77	28.77	28.77	28.77
15.24	15.24	15.24	15.24	15.24	15.24
52.8	52.8	52.8	52.8	52.8	52.8

4662	4662	4662	4662	4662	4662
31.2	31.2	31.2	31.2	31.2	31.2
16.1	16.1	16.1	16.1	16.1	16.1
55.9	55.9	55.9	55.9	55.9	55.9

4861	4861	4861	4861	4861	4861
28.77	28.77	28.77	28.77	28.77	28.77
15.24	15.24	15.24	15.24	15.24	15.24
52.8	52.8	52.8	52.8	52.8	52.8

4861	4861	4861	4861	4861	4861
28.77	28.77	28.77	28.77	28.77	28.77
15.24	15.24	15.24	15.24	15.24	15.24
52.8	52.8	52.8	52.8	52.8	52.8

4861	4861	4861	4861	4861	4861
28.77	28.77	28.77	28.77	28.77	28.77
15.24	15.24	15.24	15.24	15.24	15.24
52.8	52.8	52.8	52.8	52.8	52.8

4861	4861	4861	4861	4861	4861
28.77	28.77	28.77	28.77	28.77	28.77
15.24	15.24	15.24	15.24	15.24	15.24
52.8	52.8	52.8	52.8	52.8	52.8

4861	4861	4861	4861	4861	4861
28.77	28.77	28.77	28.77	28.77	28.77
15.24	15.24	15.24	15.24	15.24	15.24
52.8	52.8	52.8	52.8	52.8	52.8

4861	4861	4861	4861	4861	4861
28.77	28.77	28.77	28.77	28.77	28.77
15.24	15.24	15.24	15.24	15.24	15.24
52.8	52.8	52.8	52.8	52.8	52.8

5769	5769	5769	5769	5769	5769
23.10	23.10	23.10	23.10	23.10	23.10
12.38	12.38	12.38	12.38	12.38	12.38
42.92	42.92	42.92	42.92	42.92	42.92

5893	5893	5893	5893	5893	5893
22.32	22.32	22.32	22.32	22.32	22.32
11.96	11.96	11.96	11.96	11.96	11.96
41.47	41.47	41.47	41.47	41.47	41.47

6025	6025	6025	6025	6025	6025
21.54	21.54	21.54	21.54	21.54	21.54
11.55	11.55	11.55	11.55	11.55	11.55
40.02	40.02	40.02	40.02	40.02	40.02

5004	5004	5004	5004	5004	5004
28.60	28.60	28.60	28.60	28.60	28.60
15.33	15.33	15.33	15.33	15.33	15.33
53.13	53.13	53.13	53.13	53.13	53.13

5086	5086	5086	5086	5086	5086
27.66	27.66	27.66	27.66	27.66	27.66
14.83	14.83	14.83	14.83	14.83	14.83
51.39	51.39	51.39	51.39	5	

*Temperature 134°. Density 0.9258.*

$\lambda$ .....	6708	6563	6364	6147	6025	5893	5769	5679	5508
$\alpha$ ( $l=2$ -dem.) .....	18.06	18.69	19.75	20.83	21.59	22.36	23.10	23.63	24.39
$[\alpha]$ .....	9.75	10.10	10.67	11.25	11.66	12.07	12.48	12.76	13.17
$[M]$ .....	33.81	34.98	36.97	38.99	40.41	41.85	43.24	44.23	45.66
$\lambda$ .....	5461	5323	5219	5154	5086	5004	4861	4662	4359
$\alpha$ ( $l=2$ -dem.) .....	25.12	26.16	26.90	27.49	28.00	28.69	29.60	30.7	32.1
$[\alpha]$ .....	13.56	14.13	14.53	14.85	15.12	15.49	15.98	16.6	17.3
$[M]$ .....	47.02	48.97	50.35	51.46	52.41	53.71	55.41	57.5	60.1

*Temperature 149°. Density 0.914.*

$\lambda$ .....	6708	6563	6364	6147	6025	5893	5769	5679	5568
$\alpha$ ( $l=1$ -dem.) .....	8.94	9.30	9.79	10.37	10.73	11.10	11.52	11.77	12.18
$[\alpha]$ .....	9.78	10.17	10.71	11.35	11.74	12.14	12.60	12.88	13.33
$[M]$ .....	33.8	35.2	37.05	39.25	40.6	42.0	43.6	44.55	46.1
$\lambda$ .....	5461	5323	5219	5154	5086	5004	4861	4662	4359
$\alpha$ ( $l=1$ -dem.) .....	12.53	13.16	13.59	13.81	14.06	14.34	14.79	15.4	16.2
$[\alpha]$ .....	13.71	14.40	14.77	15.11	15.38	15.69	16.18	16.9	17.7
$[M]$ .....	47.4	49.8	51.1	52.23	53.2	54.23	56.0	58.5	61.3

*Temperature 168°. Density 0.8995.*

$\lambda$ .....	6708	6563	6364	6147	6025	5893	5769	5679	5568
$\alpha$ ( $l=2$ -dem.) .....	17.41	18.10	19.12	20.33	21.00	21.80	22.65	23.17	23.91
$[\alpha]$ .....	9.68	10.06	10.63	11.30	11.67	12.12	12.69	12.88	13.29
$[M]$ .....	33.50	34.89	36.84	39.17	40.46	42.00	43.64	44.64	46.06
$\lambda$ .....	5461	5323	5219	5154	5086	5004	4861	4662	4359
$\alpha$ ( $l=2$ -dem.) .....	24.62	25.53	26.41	27.03	27.49	28.19	29.15	30.3	31.4
$[\alpha]$ .....	13.69	14.19	14.68	15.03	15.28	15.67	16.20	16.8	17.4
$[M]$ .....	47.43	49.19	50.88	52.08	52.96	54.31	56.16	58.4	60.5



*Temperature 112°. Density 0.9292.*

$\lambda$ .....	6708	6563	6364	6147	6025	5893	5769	5679	5568
$\alpha$ ( $l=2$ -dem.) .....	16.54	17.20	18.12	19.24	19.88	20.56	21.26	21.80	22.44
$[\alpha]$ .....	8.90	9.26	9.75	10.35	10.70	11.06	11.44	11.73	12.07
$[\mathbf{M}]$ .....	33.35	34.68	36.63	38.81	40.08	41.47	42.87	43.95	45.24
$\lambda$ .....	5461	5323	5219	5154	5086	5004	4861	4662	
$\alpha$ ( $l=2$ -dem.) .....	23.08	23.92	24.76	25.25	25.56	26.04	26.94	27.9	
$[\alpha]$ .....	12.42	12.87	13.32	13.59	13.75	14.01	14.50	15.0	
$[\mathbf{M}]$ .....	46.54	48.23	49.92	50.91	51.53	52.50	54.32	56.3	

*Temperature 132°. Density 0.9140.*

$\lambda$ .....	6708	6563	6364	6147	6025	5893	5769	5679	5568
$\alpha$ ( $l=2$ -dem.) .....	16.53	17.17	18.11	19.21	19.86	20.59	21.30	21.82	22.49
$[\alpha]$ .....	9.04	9.39	9.91	10.51	10.87	11.26	11.65	11.93	12.30
$[\mathbf{M}]$ .....	33.88	35.20	37.12	39.38	40.71	42.20	43.66	44.72	46.10
$\lambda$ .....	5461	5323	5219	5154	5086	5004	4861	4662	
$\alpha$ ( $l=2$ -dem.) .....	23.17	23.89	24.80	25.20	25.74	26.35	27.34	28.5	
$[\alpha]$ .....	12.68	13.07	13.57	13.78	14.08	14.42	14.96	15.6	
$[\mathbf{M}]$ .....	47.49	48.97	50.83	51.65	52.76	54.01	56.04	58.5	

*Temperature 145°. Density 0.9035.*

$\lambda$ .....	6563	6364	6147	6025	5893	5769	5679	5568
$\alpha$ ( $l=2$ -dcm.)	17.01	17.95	19.11	19.77	20.50	21.20	21.71	22.41
$[\alpha]$ .....	9.41	9.93	10.58	10.94	11.34	11.73	12.01	12.40
$[\eta]$ .....	35.27	37.22	39.63	40.99	42.51	43.96	45.02	46.47
$\lambda$ .....	5323	5219	5154	5086	5004	4861	4662	
$\alpha$ ( $l=2$ -dcm.)	23.89	24.69	25.15	25.66	26.17	27.24	28.5	
$[\alpha]$ .....	13.22	13.66	13.92	14.20	14.48	15.07	15.8	
$[\eta]$ .....	49.54	51.20	52.15	53.20	54.27	56.48	59.1	

*Temperature 165°. Density 0.887.*

$\lambda$ .....	6563	6364	6147	6025	5893	5769	5679	5568
$\alpha$ ( $l=2$ -dcm.)	16.70	17.65	18.70	19.39	20.10	20.82	21.39	22.09
$[\alpha]$ .....	9.41	9.95	10.54	10.93	11.33	11.74	12.06	12.45
$[\eta]$ .....	35.27	37.28	39.50	40.96	42.46	43.98	45.18	46.66
$\lambda$ .....	5323	5219	5154	5086	5004	4861	4662	
$\alpha$ ( $l=2$ -dcm.)	23.59	24.37	24.85	25.28	25.80	26.68	28.4	
$[\alpha]$ .....	13.30	13.74	14.01	14.25	14.54	15.04	16.0	
$[\eta]$ .....	49.83	51.47	52.49	53.40	54.49	56.37	60.0	

# [IV.—*The Tannin of the Canadian Hemlock* (*Tsuga Canadensis*, Carr.).

By RODGER JAMES MANNING and MAXIMILIAN NIERENSTEIN.

ALTHOUGH the chemistry of the pyrogallol tannins, of which gallotannin is the best known representative, has progressed during the last fifteen years, little or nothing has been published on the catechol (phlobaphen-producing) tannins, to which group nearly all the technically important vegetable tanning materials belong. We have investigated hemlock tannin, a representative of this group, in view of its colonial importance, and have accumulated observations during the three and a-half years this work has been in progress which we describe in this paper, without, however, attempting to draw any conclusions as to the probable constitution of hemlock tannin. Those who are acquainted with the literature on gallotannin (compare Dekker, "De Looistoffen," 1906; Nierenstein, "Chemie der Gerbstoffe," 1910; Dekker, "Die Gerbstoffe," 1913; Perkin and Everest, "The Natural Organic Colouring Matters," 1918) will be struck by the numerous formulæ which have been suggested for gallotannin, and the contradictory results that have been obtained. This is due to the amorphous character of gallotannin in particular and the tannins in general, and it is for this reason that we give our results on hemlock tannin without committing ourselves at this juncture to any theoretical discussion on the subject.

## *Bötttinger's Bromo-hemlock Tannin.*

Bötttinger (*Ber.*, 1884, 17, 1041) examined the action of bromine on tannin extracts, and determined the percentage of bromine contained in the precipitated bromo-compounds. On the basis of the bromo-compounds obtained from mangrove, hemlock, quebracho, mimosa, chestnut, *Terra japonica*, and spruce, he proposed formulæ for these tannins which are more or less generally accepted. Bötttinger's formula for hemlock tannin is  $C_{20}H_{18}O_{10}$ ; he deduced this from his bromo-derivative,  $C_{20}H_{14}O_{10}Br_4$ , from which he also prepared the acetyl derivative,  $C_{20}H_9O_{10}Br_4Ac_5$ . We have made a careful re-investigation of Bötttinger's work on hemlock tannin, with the following results:

(1) Bötttinger's bromination method does not always yield the same product,  $C_{20}H_{14}O_{10}Br_4$ , which requires  $Br = 43.60$  per cent.,

but a series of compounds in which the bromine content varies from 40 to 49 per cent. The analyses of eleven preparations gave:

Br = 41.28, 47.56, 43.88, 40.12, 43.20, 47.29, 44.56, 41.74, 48.48, 41.56, and 43.26 per cent.

(2) If Böttlinger's product is obtained, it can be fractionated into a number of compounds in which the bromine content varies from 40 to 48 per cent. The fractionation method employed by us consisted in dissolving the bromo-compound in acetone and fractionally precipitating by the addition of chloroform. Three such experiments were made, and the results were:

*Experiment I.*—Bromine content of product, 43.12 per cent.

Fractions:	I.	II.	III.	IV.	V.
Br =	43.56	45.63	46.82	46.96	48.09 per cent.

*Experiment II.*—Bromine content of product, 43.88 per cent.

Fractions:	I.	II.	III.	IV.	V.
Br =	40.22	42.84	44.22	47.86	48.56 per cent.

*Experiment III.*—Bromine content of product, 43.98 per cent

Fractions:	I.	II.	III.
Br =	41.98	44.56	46.22 per cent.

(3) If hemlock tannin is prepared and fractionated by the method described later, and the different fractions are brominated separately, a series of bromo-compounds is obtained in which the bromine content increases as the phlobaphen content decreases.

Brominated Phlobaphens.			Brominated Hemlock Tannin.			
Frac-tions:	I.	II.	Frac-tions:	I.	III.	V.
Br =	38.59	42.33%	Br =	43.56	46.82	47.40%
Br =	39.14	41.56%	Br =	—	46.77	48.09%
Br =	40.11	42.82%	Br =	—	46.96	48.22%
Br =	—	—	Br =	—	—	49.56%

Our results suggest that Böttlinger's formula for hemlock tannin and bromo-hemlock tannin must be disregarded, which conclusion, probably, also applies to the other bromo-tannins mentioned.

#### *Alkali Hydrolysis of Bromo-hemlock Tannin.*

During his investigations on bromo-quebracho tannin, Nierenstein (*Collegium*, 1905, 69) obtained on hydrolysis with alcoholic potassium hydroxide (1) *isovanillic* acid, and (2) a substance,  $C_8H_7O_4Br$ , to which he assigned provisionally the name monobromo-quebrachilic acid. The latter crystallised from chloroform in small needles melting at 119–120°. We have extended these investi-

gations to bromo-hemlock tannin, but were only able to isolate a substance,  $C_8H_7O_4Br$ , which apparently is closely allied to monobromoquebrachilic acid, and is provisionally called *monobromotsuginic acid*. For comparison, the melting points of these two substances and of their derivatives are tabulated.

<i>Monobromoquebrachilic Acid.</i>		<i>Monobromotsuginic Acid.</i>	
Free acid ...	m. p. 119—120°	Free acid ...	m. p. 143—145°
Methyl ester	m. p. 96—98°	Methyl ester	m. p. 108—111°
Ethyl ester...	m. p. 93—94°	Ethyl ester	m. p. 100—102°

Nierenstein (*loc. cit.*) obtained from monobromoquebrachilic acid on further hydrolysis monobromoresorcinol, but we have failed to isolate any definite disintegration product from monobromotsuginic acid.

*Alkali Hydrolysis.*—About 10 grams of bromo-hemlock tannin containing 44.56 per cent. of bromine were heated under reflux on a water-bath with 100 c.c. of 20 per cent. alcoholic potassium hydroxide for six hours, and the solution was filtered after dilution with water. The filtrate was evaporated to dryness and extracted with acidified boiling alcohol. After several days, a crop of needles (about 0.1 gram) was obtained, which was collected and recrystallised from alcohol and benzene. Repetition of the hydrolysis gave amounts of crude monobromotsuginic acid varying from 0.7 to 1.2 per cent. of the weight of bromo-hemlock tannin.

*Monobromotsuginic acid* crystallises from alcohol and benzene in small, sharp needles which melt at 143—145°, carbon dioxide being evolved.

Found: C=38.75; H=3.42; Br=31.62. M.W.=251.

$C_8H_7O_4Br$  requires C=38.87; H=2.87; Br=32.39 per cent.  
M.W.=247.

The *methyl* ester, prepared by the hydrochloric acid method, crystallises from chloroform in silky needles melting at 108—111°.

Found: C=41.95; H=3.67.

$C_9H_9O_4Br$  requires C=41.38; H=3.44 per cent.

The *ethyl* ester crystallises from alcohol in needles melting at 100—102°.

Found: C=43.22; H=4.58.

$C_{10}H_{11}O_4Br$  requires C=43.63; H=4.00 per cent.

The *acetyl* derivative is prepared by digesting monobromotsuginic acid with acetic anhydride for several hours, the excess of acetic anhydride being removed in a vacuum. It separates from



alcohol in small, cubic crystals melting at 124—126°, carbon dioxide being evolved.

Found: C=41.22; H=3.64.

$C_{10}H_9O_5Br$  requires C=41.52; H=3.12 per cent.

Attempts to prepare carbethoxy- and benzoyl derivatives failed, as the products did not crystallise.

So far as it is possible to deduce from the above data, monobromotsuginic acid may be regarded as having the constitution  $CO_2H \cdot C_7H_5OBr \cdot OH$ .

Much work, however, is still required before it will be possible to decide on a definite constitution for this fission product, which in time may prove of importance to the chemistry of hemlock tannin in particular and the catechol tannins in general.

#### *Preparation of Hemlock Tannin.*

The finely sieved hemlock bark (about 8 kilos. were used each time) was extracted repeatedly with acetone. The extraction must always be carried out in the cold, on account of the ease with which hemlock tannin is oxidised to phlobaphens. The united acetone solutions were evaporated to one-third of their bulk under diminished pressure at about 55°. In this and in the succeeding operations, great care must be taken to keep the temperature as low as possible, as otherwise a considerable loss of hemlock tannin occurs through the formation of phlobaphen.

In order to precipitate the phlobaphens, the concentrated acetone solution was poured into twice its bulk of water and allowed to remain overnight. The phlobaphens, which appeared as a bulky, dark red mass, were collected, washed, and dried in a desiccator. The filtrate, which contained the hemlock tannin and always a certain amount of unprecipitated phlobaphens, was evaporated to a viscid mass in a vacuum at a temperature not exceeding 55°. This was dissolved in 570 c.c. of alcohol, and if still rich in phlobaphens gave a further precipitation if diluted with an equal amount of water. Usually, only a small portion of the alcoholic solution was tested, so as to avoid loss through oxidation. If, then, on adding water to a test portion little or no precipitation of phlobaphens took place, the whole alcoholic solution was evaporated to dryness under diminished pressure at 55°. On the other hand, if much phlobaphen was precipitated, the solution was diluted with an equal amount of water, and the preceding operations were repeated. The resultant mass (about 300 grams) was

carefully dried, and appeared then as a dark red, brittle substance, evidently still rich in phlobaphens.

The crude hemlock tannin (100 grams) was extracted with 750 c.c. of carefully dried acetone. The acetone was added in several portions and filtered before each fresh addition. The residue insoluble in acetone appeared, when carefully washed with light petroleum and dried in a vacuum at 70°, as a pale brown powder, which weighed about 5 grams. The dark red acetone solution was treated with portions of 50, 100, and 400 c.c. of chloroform, as used by Nierenstein in the purification of gallotannin (*Annalen*, 1912, **388**, 243). The first two fractions were dark and inclined to be viscid. The third fraction was pink. When washed with light petroleum and dried in a vacuum, they weighed respectively 8, 12, and 35 grams. The filtrate from fraction III was evaporated to dryness under diminished pressure at 55°, and the residue dissolved in 150 c.c. of ethyl acetate, which when poured into 200 c.c. of chloroform yielded 26 grams of a light-coloured precipitate. The filtrate was again evaporated to dryness, the residue dissolved in 100 c.c. of ethyl acetate, and fractions V and VI were precipitated by successive addition of 100 c.c. of chloroform. Fraction V (10 grams) was faintly pink, whilst fraction VI (2 grams) was creamy-white.

Found:

Fraction III.—C=61.58, 61.86; H=5.05, 5.29.

Fraction IV.—C=63.52, 63.30; H=5.31, 5.33.

Fraction V.—C=64.09; H=5.41.

Fraction VI.—C=64.24, 64.06, 64.33; H=4.88, 5.08, 5.23 per cent.

The amorphous character of the products and also the variations in the composition of the different fractions show how undesirable it is to calculate an empirical formula for hemlock tannin, as is also the case with gallotannin (compare Nierenstein, *Annalen*, 1912, **388**, 243). In addition to this, hemlock tannin also contains traces of a methoxy-compound, from which we have not succeeded in freeing it. We found that even the purest fraction (VI) contained  $\text{OMe}=0.80$ , whilst some of the other fractions gave as much as 3.56 per cent. of methoxyl.\*

\* During these investigations, experiments were also made to see if some of the methoxyl in the hemlock tannin showed resistance towards hydriodic acid, and we therefore re-heated the Perkin-Zeisel apparatus on the following day after the methoxy-estimations had been carried out, as described by Herzig (*Monatsh.*, 1905, **25**, 603; 1908, **29**, 263) during his investigation of ellagic acid. We were thus able to observe an increase in the methoxy-content which, however, could be accounted for by the formation of a

Purified hemlock tannin is a pink, amorphous powder which does not melt when heated above  $300^{\circ}$ , but begins to decompose at about  $260$ – $275^{\circ}$ . It is soluble in alcohol, acetone, ethyl acetate, or water, in which it forms deep red solutions. When hydrolysed according to Fischer and Freudenberg's method (*Ber.*, 1912, **45**, 915) for the estimation of sugar in gallotannin, it was found that hemlock tannin does not contain any kind of sugar. With iron chloride it gives a deep green coloration, especially in alcoholic solution. Hemlock tannin is precipitated by gelatin or alkaloids, and is quantitatively absorbed by caseinogen (compare Körner and Nierenstein, *Chem. Zeit.*, 1911, **36**, 31; Nierenstein, *Annalen*, 1912, **388**, 224; Spiers, *J. Agric. Sci.*, 1919, **6**, 77).

#### *Alkali Hydrolysis of Hemlock Tannin.*

(1) *Alcoholic Potassium Hydroxide*.—The only definite fission product obtained by this method was protocatechuic acid, crystallising from water in small needles melting at  $191$ – $194^{\circ}$ , carbon dioxide being evolved. When mixed with protocatechuic acid, no depression (m. p.  $193$ – $194^{\circ}$ ) was observed.

(2) *Alcoholic Barium Hydroxide*.—We originally used aqueous barium hydroxide with some success, but later employed the methyl-alcoholic solution (compare Müller, T., 1915, **107**, 874). This hydrolysis yielded protocatechuic acid, 2:3-dihydroxybenzoic acid, and a new substance,  $C_{10}H_8O_3$ , which was apparently an *aldehyde*.

The hydrolysis was carried out by heating about 10 grams of hemlock tannin with an excess of methyl-alcoholic barium hydroxide for eight to ten hours under reflux. The alcohol was then removed on the water-bath, and the residue diluted with water and acidified with dilute sulphuric acid. The liquid, and also the barium sulphate precipitate, were extracted several times with ether, and the ethereal solution (solution A) treated with sodium hydrogen carbonate solution saturated with carbon dioxide. The aqueous part thus obtained was acidified and extracted with ether (solution B), and both ethereal solutions were investigated separately.

*Ethereal Solution A*.—The solution left, on evaporation, a tarry precipitate of silver iodide when hydriodic acid and acetic anhydride are left for twenty-four hours and then heated (Manning and Nierenstein, *Ber.*, 1913, **46**, 3983. Critics of this note (compare G. Goldschmidt, *Ber.*, 1914, **47**, 389; A. G. Perkin and Oesch, T., 1914, **105**, 2352) appear to have overlooked the necessity of allowing the mixture to remain for at least a day before any precipitation of silver iodide can be obtained.

mass, which became solid on rubbing and kneading with light petroleum. The dry solid was then extracted in a Soxhlet apparatus with benzene, when the greater part of the product dissolved, leaving a tarry residue in the thimble. The benzene was evaporated to dryness, and the residue (about 0.8 gram) crystallised from alcohol and benzene, from which it separated in small, silky plates melting at 125—126°. It is also soluble in alcohol or much benzene or toluene, from which solutions it crystallises in needles (m. p. 125—126°) after strong concentration of the solvents.

Found: C=68.45; H=4.83. M.W.=160, 166.

$C_{10}H_8O_3$  requires C=68.18; H=4.54 per cent. M.W.=176.

With phenylhydrazine it forms a *phenylhydrazone*, which crystallises from glacial acetic acid in dark brown needles melting and decomposing at 191°.

Found: N=17.91, 17.49.

$C_{16}H_{10}O_2N_2$  requires N=17.27 per cent.

When oxidised on the water-bath with potassium permanganate in alkaline suspension, it yields the *acid*,  $C_9H_7O_2 \cdot CO_2H$ , which crystallises from water in long, prismatic needles melting at 214—216°, carbon dioxide being evolved.

Found: C=62.42; H=4.60.

$C_{10}H_8O_4$  requires C=62.50; H=4.20 per cent.

The *sodium* and *potassium* salts were prepared and crystallised from water.

Found: Na=11.12; K=20.86.

Calculated: Na=10.74; K=20.40 per cent.

Diazomethane yields the *methyl* ester, which crystallises from benzene in silky needles melting at 152—153°.

Found: C=64.24; H=4.82.

$C_{11}H_{10}O_4$  requires C=64.18; H=4.62 per cent.

*Ethereal Solution B.*—The residue which was left on evaporation of the ether crystallised from water in small needles melting indefinitely between 145° and 168°, although the product was recrystallised several times from that solvent. The only definite colour reactions obtained were those of protocatechuic acid, and the analytical data also agreed for a dihydroxybenzoic acid. (Found: C=54.12; H=4.22.  $C_7H_6O_4$  requires C=54.52; H=3.94 per cent.) Attempts were made to separate the mixture by fractional crystallisation, but no fraction of a definite melting point was obtained. The product when heated with soda-lime only gave, so far as could be ascertained, catechol (small needles from

benzene, m. p. 102—103°), from which we concluded that the mixture consisted probably of protocatechuic acid (m. p. 198—199°) and 2:3-dihydroxybenzoic acid (m. p. 204°) (compare Praxmarer, *Monatsh.*, 1906, **27**, 1199; also abstract of this paper, A., 1907, **92**, i, 216, where the melting point is wrongly given as 240°). The product was therefore treated in ethereal solution with diazomethane and converted into the methyl esters of veratric acid (m. p. 59—60°) and 2:3-dimethoxybenzoic acid (m. p. 57—58°) (compare Praxmarer, *loc. cit.*), and the mixture fractionated under diminished pressure. Sixteen grams of the methyl esters gave the following fractions, which crystallised from benzene on subsequent solidification:

Fraction I.—1.84 Grams, b. p. 124—127°/10—11 mm., m. p. 47—53°.

Fraction II.—4.26 Grams., b. p. 124—126°/10—12 mm., m. p. 52—54°.

Fraction III.—4.47 Grams, b. p. 125—127°/10—12 mm., m. p. 55—56°.

Fraction IV.—2.12 Grams, b. p. 126—129°/10—11 mm., m. p. 58—59°.

Each fraction was hydrolysed on the water-bath with alkali, and the free methoxy-acids were crystallised from dilute alcohol. These fractions melted as follows:

Fraction I.—M. p. 162—168°.

Fraction II.—M. p. 178—180°. Mixed m. p. with veratric acid, 178—180°; mixed m. p. with 2:3-methoxybenzoic acid, 158—164°.

Fraction III.—M. p. 176—183°. Mixed m. p. with veratric acid, 164—171°; mixed m. p. with 2:3-dimethoxybenzoic acid, 172—178°.

Fraction IV.—M. p. 184—186°. Mixed m. p. with veratric acid, 168—174°; mixed m. p. with 2:3-dimethoxybenzoic acid, m. p. 183—185°.

The melting point of veratric acid is given as 181° (compare Freund and Niederhofheim, *Ber.*, 1896, **29**, 858; Kostanecki and Tambor, *Ber.*, 1907, **39**, 4022). There is, however, no reference to 2:3-dimethoxybenzoic acid. This was therefore prepared by the action of diazomethane on 2:3-dihydroxybenzoic acid prepared according to Praxmarer's method (*loc. cit.*); the ester was subsequently hydrolysed and the methoxy-acid crystallised from dilute alcohol, from which it separated in needles melting at 187—188°, carbon dioxide being evolved. (Found: C=59.14; H=5.72.  $C_9H_{10}O_4$  requires C=59.31; H=5.54 per cent.)

From the above data, it is probable that fraction II consisted mainly of veratric acid (Found: C=59.12; H=5.78. Calc.: C=59.31; H=5.54 per cent.), whereas fraction IV consisted of 2:3-dimethoxybenzoic acid (Found: C=58.92; H=5.46. Calc.: C=59.31; H=5.54 per cent.), from which we conclude that protocatechuic and 2:3-dihydroxybenzoic acids are formed during the hydrolysis of hemlock tannin.

#### *Methylated Hemlock Tannin.*

Hemlock tannin was methylated with diazomethane in ethereal suspensions, fractions IV, V, and VI only being used for the methylation. The dry tannin was suspended in ether, as used in the Grignard reaction (compare Clibbens and Nierenstein, T., 1915, 107, 1491), and an excess of diazomethane allowed to act on it for about twelve hours. In the case of fraction IV there was always a residue, after methylation, insoluble in ether [similar observations were made by Herzig (*Monatsh.*, 1912, **33**, 843), and Fischer and Freudenberg (*Ber.*, 1912, **45**, 2723), during the methylation of gallotannin with diazomethane]. Fraction V also left a small residue, but fraction VI on methylation dissolved completely in ether.

The ethereal solution was filtered and the ether removed under diminished pressure. The residue was purified by dissolving in a little alcohol and pouring into water. It frequently happened that the methylated product did not separate out readily, in which case the liquid was shaken vigorously to coagulate the precipitate and allowed to remain for a time. The precipitate was then collected, carefully washed, and dried in a desiccator.

Methylated hemlock tannin obtained in this way after several precipitations was a white, amorphous product with a more or less distinctly yellow tint; it was readily soluble in alcohol, ether, acetone, benzene, carbon tetrachloride, or *s*-tetrachloroethane, but insoluble in light petroleum. The product had no definite melting point; it sintered at 74–79° and melted at 134–141°.

Found: C=65.69, 65.25, 64.82, 65.12; H=5.58, 5.46, 5.82, 5.27; OMe=26.48, 25.65, 25.84 per cent. M.W. (in chloroform)=620, 561, 552, 574.

The methoxy-estimations were carried out in a Zeisel-Perkin apparatus, acetic anhydride being added. If the latter was replaced by phenol (compare Weishut, *Monatsh.*, 1913, **33**, 1165), the same result was obtained (OMe=25.76 per cent.). In view of the experiences of W. Richter (*Diss.*, Erlangen, 1902, 44), who found that eutannin is more fully methylated with diazomethane

in an acetone solution than in an ethereal one, we also used the former as a solvent, without, however, increasing the methoxy-content. (Found: OMe=25.89 per cent.). For similar reasons, we also used methyl alcohol as a solvent, (compare Geake and Nierenstein, *Biochem. J.*, 1914, **8**, 292), the result being the same (Found: OMe=25.43 per cent.).

Methylated hemlock tannin was found to be optically active:  $[\alpha]_D^{25} -41^\circ$  (in chloroform),  $-24.7^\circ$  (in *s*-tetrachloroethane),  $50.1^\circ$  (in alcohol), and  $-16.9^\circ$  (in acetone).

#### *Alkali Hydrolysis of Methylated Hemlock Tannin.*

Methylated hemlock tannin (about 5—10 grams) was hydrolysed by boiling with a 10 per cent. solution of alcoholic potassium hydroxide for about three hours. The alcohol was then evaporated, and the residue extracted with boiling water and filtered from any incompletely hydrolysed or tarry substance. On acidifying with dilute sulphuric acid, the filtrate gave a bulky precipitate (precipitate A), which was collected, washed, and dried in a desiccator. The filtrate was extracted with ether several times, and the ethereal extract treated with a 5 per cent. solution of sodium hydrogen carbonate saturated with carbon dioxide. Nothing was found to remain in the ether. The sodium hydrogen carbonate solution was acidified with dilute sulphuric acid and extracted with ether. On evaporation of the ether, a residue was obtained which was crystallised several times from water with the addition of animal charcoal, when small crystals were obtained melting at  $208^\circ$ . They proved to be vanillic acid, and gave no depression of the melting point when mixed with vanillic acid. (Found: C=57.02; H=5.08. Calc.: C=57.11; H=4.81 per cent.)

*Precipitate A.*—The product was purified by dissolving several times in alcohol and precipitating with water.

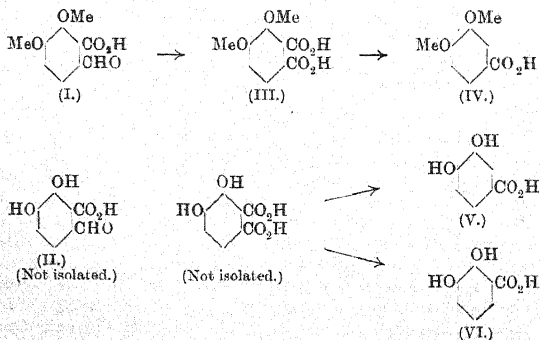
Found: C=67.14, 66.83; H=6.49, 6.22; OMe=28.18 per cent.

When oxidised with potassium permanganate in alkaline solution, hemipinic acid was produced. The following method of oxidation gave the best results. 1.5 Grams of the substance were heated on a water-bath for six to eight hours with 75 c.c. of 2*N*-potassium hydroxide and 3 grams of potassium permanganate dissolved in about 50 c.c. of water, which were added in two portions. The solution was acidified, filtered, and extracted with ether. The residue left on evaporation crystallised from water in small needles, which melted when slowly heated at  $170$ — $173^\circ$  (compare Nierenstein, *Annalen*, 1913, **396**, 198; Pschorr and

Samuleanu, *Ber.*, 1899, **32**, 3411), which melting point was not depressed when mixed with hemipinic acid prepared from opianic acid. (Found: C=53.33; H=5.09. Calc.: C=53.07; H=4.47 per cent.)

Mild hydrolysis of precipitate A furnished opianic acid, which was obtained on warming 2 grams of the substance with 20 c.c. of 2*N*-alcoholic potassium hydroxide for several hours on the water-bath under reflux at a temperature not higher than 60°. The alcohol was evaporated, the residue acidified, and extracted with ether. The ethereal extract was shaken with sodium hydrogen carbonate solution saturated with carbon dioxide, and the aqueous part, after acidification with dilute sulphuric acid, extracted with ether. The carefully dried residue which was left on evaporation of the ether deposited, from benzene, thin, prismatic needles melting at 147–149°. When mixed with opianic acid, no depression of the melting point was observed. (Found: C=56.82, 56.78; H=5.12, 4.94. Calc.: C=57.11; H=4.81 per cent.) A small amount was converted into the oxime, crystallising in small needles melting at 81°, which is in the vicinity of the melting point 82–83°, as found by W. H. Perkin, jun. (*T.*, 1890, **57**, 1071). There was not enough material for a combustion.

The fact that the methylated hemlock tannin yields opianic acid (I) suggests the possible existence of noropianic acid (II) in hemlock tannin, which probably explains the formation of hemipinic acid (III) and veratric acid (IV) from methylated hemlock tannin and protocatechuic acid (V) and 2:3-dihydroxybenzoic acid (VI) from hemlock tannin:





In conclusion, we wish to take this opportunity of expressing our thanks to the Research Fund Committee of the Chemical Society, and to the Colston Society of the University of Bristol, for grants towards this investigation. We also wish to thank Messrs. Davis and Sons, Tanners, Kingston, Canada, for a generous supply of hemlock bark.

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### LV.—*The Formation of Diazoamino-compounds from $\beta$ -Naphthylamine.*

By GEORGE MARSHALL NORMAN.

DURING the preparation of some diazoamino-compounds involving the action of diazotised  $\beta$ -naphthylamine on amines of the benzene series, it was noticed that, in the case of *o*-toluidine, the product was a tarry substance which, on keeping, became a dark red solid and consisted of *o*-tolueneazo- $\beta$ -naphthylamine (Norman, T., 1912, 101, 1914).

A search has been made for other cases of this result, and as both *m*- and *p*-toluidine gave diazoamino-compounds, *o*-substituted amines have been selected for the purpose. However, a substituent in the *o*-position, even a methyl radicle, is not the only condition necessary, for, although *m*-4-xylydine gave *m*-xylene-4-azo- $\beta$ -naphthylamine, *p*-xylydine gave a diazoamino-compound, a result also obtained with *o*-chloroaniline, 3-bromo-*p*-toluidine, and 5-bromo-*o*-toluidine. Under the same conditions, diazotised  $\beta$ -naphthylamine does not appreciably react with 3-nitro-*p*-toluidine or 5-nitro-*o*-toluidine, even on keeping for several hours. The same difficulty was encountered in the case of *s*-trichloroaniline.

The diazoamino-compounds obtained pass quite readily into the isomeric aminoazo-compounds on heating with the contained benzene base and its hydrochloride. This can be explained by the occurrence of an intramolecular change or by a preliminary decomposition into a diazonium salt and  $\beta$ -naphthylamine, with subsequent recombination to form the azo-compound, and this is supported by the formation of *p*-tolueneazo- $\beta$ -naphthylamine on heating diazoamino-*p*-toluene with *p*-toluidine hydrochloride and  $\beta$ -naphthylamine in molecular proportions and excess of *p*-toluidine.

The experiments of Meldola and Streatfeild (T., 1887, **51**, 434) showed that the action of aqueous acids is to decompose mixed diazoamino-compounds into four products, the bases and the corresponding diazonium salts in molecular proportions, but under the conditions of the present experiments the only aminoazo-compound produced is derived from the diazotised benzenoid base and  $\beta$ -naphthylamine in practically quantitative yield. The decomposition into four products evidently does not occur, or one would expect to find  $\beta$ -naphthaleneazo- $\beta$ -naphthylamine among the products, unless, indeed,  $\beta$ -naphthalenediazonium chloride in the presence of the benzene base is converted into a substituted benzenediazonium chloride.

When the diazoamino-compounds are heated with  $\beta$ -naphthol, either  $\beta$ -naphthylamine or the benzene base is eliminated, and the resulting hydroxyazo-compound is not a mixture in the cases examined. Thus, the diazoamino-compound obtained from 5-bromo-*o*-toluidine gave 5-bromo-*o*-tolueneazo- $\beta$ -naphthol and eliminated  $\beta$ -naphthylamine, but the compounds from *o*-chloroaniline, 3-bromo-*p*-toluidine, and *p*-xylydine gave  $\beta$ -naphthaleneazo- $\beta$ -naphthol and eliminated the benzenoid base. Probably this can be best explained by the formation of an unstable intermediate compound, which undergoes decomposition with the elimination of one of the bases present, the mode of decomposition depending on the nature and position of the substituent radicles.

#### EXPERIMENTAL.

*m*-Xylene-4-azo- $\beta$ -naphthylamine,  $C_6H_5(CH_3)_2 \cdot N_2 \cdot C_{10}H_7 \cdot NH_2$ .

This compound crystallises from methylated spirit in orange-red plates melting at  $126^\circ$ :

0.1345 gave 18 c.c.  $N_2$  (moist) at  $16^\circ$  and 750 mm.  $N=15.4$ .

$C_{18}H_{17}N_3$  requires  $N=15.27$  per cent.

The *acetyl* derivative crystallises from ethyl acetate in small, orange-red needles melting at  $142^\circ$ :

0.1235 gave 13.9 c.c.  $N_2$  (moist) at  $15^\circ$  and 752 mm.  $N=13.1$ .

$C_{20}H_{19}ON_3$  requires  $N=13.25$  per cent.

The *benzoyl* derivative crystallises from ethyl acetate in bright red needles melting at  $145^\circ$ :

0.1142 gave 11.2 c.c.  $N_2$  (moist) at  $17^\circ$  and 756 mm.  $N=11.3$ .

$C_{26}H_{21}ON_3$  requires  $N=11.08$  per cent.

*Action of  $\beta$ -Naphthalenediazonium Chloride on m-4-Xylidine.*

On the addition of sodium acetate to the cold solution, a brown solid separated which became tarry, and, on keeping, solidified to a red solid, which was identified as *m*-xylene-4-azo- $\beta$ -naphthylamine.

*Reduction of m-Xylene-4-azo- $\beta$ -naphthylamine.*

In order to establish beyond doubt the constitution of this compound, it was reduced with zinc dust in acetic acid solution. Acetic anhydride was then added, and the subsequent addition of a little water caused the separation of a solid, which was identified as diacetyl-1:2-naphthylenediamine, whilst from the mother liquor aceto-*m*-4-xylidide was obtained.

*Action of Nitrous Acid on m-Xylene-4-azo- $\beta$ -naphthylamine.*

Meldola and East's method (T., 1888, **53**, 465) gave a tarry solid, which was boiled with alcoholic potassium hydroxide. The product was identified as *m*-xylene-4-azo- $\beta$ -naphthol (m. p. 166°).

*o-Chlorobenzeneazo- $\beta$ -naphthylamine,  $C_6H_4Cl \cdot N_2 \cdot C_{10}H_6 \cdot NH_2$ .*

This compound crystallises from benzene in red needles melting at 151°:

0.1520 gave 19.5 c.c.  $N_2$  (moist) at 16° and 748 mm.  $N=14.71$ .

$C_{10}H_{12}N_3Cl$  requires  $N=14.93$  per cent.

The *acetyl* derivative crystallises from ethyl acetate in orange-red, silky needles melting at 153°:

0.1324 gave 0.5940 AgCl.  $Cl=11.1$ .

$C_{18}H_{14}ON_3Cl$  requires  $Cl=10.97$  per cent.

The *benzoyl* derivative crystallises from glacial acetic acid in orange needles melting at 167°:

0.1841 gave 0.6955 AgCl.  $Cl=9.35$ .

$C_{28}H_{16}ON_3Cl$  requires  $Cl=9.2$  per cent.

 *$\beta$ -Naphthalenediazoamino-o-chlorobenzene,  $C_6H_4Cl \cdot N_3H \cdot C_{10}H_7$ .*

This compound crystallises from toluene in pale brown, minute needles melting at 100°. When heated with *o*-chloroaniline and its hydrochloride at 60°, it changes readily into the isomeric amino-azo-compound, and when heated with  $\beta$ -naphthol it gives  $\beta$ -naphthaleneazo- $\beta$ -naphthol and *o*-chloroaniline:

0.1231 gave 15.9 c.c.  $N_2$  (moist) at  $17^\circ$  and 750 mm.  $N=14.8$ .  
 $C_{16}H_{12}N_3Cl$  requires  $N=14.93$  per cent.

*3-Bromo-p-tolueneazo-β-naphthylamine*,  $C_6H_3MeBr \cdot N_2 \cdot C_{10}H_6 \cdot NH_2$ .

This compound crystallises from methylated spirit in glistening, dark red plates melting at  $172^\circ$ :

0.1461 gave 16.0 c.c.  $N_2$  (moist) at  $18^\circ$  and 752 mm.  $N=12.48$ .  
 $C_{17}H_{14}N_3Br$  requires  $N=12.35$  per cent.

The *acetyl* derivative crystallises from glacial acetic acid in small, yellow needles melting at  $168^\circ$ :

0.1324 gave 0.6459 AgBr.  $Br=20.76$ .  
 $C_{19}H_{16}ON_3Br$  requires  $Br=20.94$  per cent.

The *benzoyl* derivative crystallises from ethyl acetate in orange-red needles melting at  $186^\circ$ :

0.1448 gave 0.6090 AgBr.  $Br=17.89$ .  
 $C_{24}H_{18}ON_3Br$  requires  $Br=18.02$  per cent.

*4-β-Naphthalenediazoamino-3-bromotoluene*,  
 $C_6H_3MeBr \cdot N_3H \cdot C_{10}H_7$ .

This compound crystallises from methylated spirit in pale brown prisms melting at  $104^\circ$ . On heating with 3-bromo-*p*-toluidine and its hydrochloride at  $60^\circ$ , it passes readily into the isomeric amino-azo-compound, and when heated with  $\beta$ -naphthol eliminates 3-bromo-*p*-toluidine and gives 3-bromo-*p*-tolueneazo- $\beta$ -naphthol, which crystallises from benzene in red needles melting at  $169^\circ$ :

0.23 gave 24 c.c.  $N_2$  (moist) at  $14^\circ$  and 752 mm.  $N=12.14$ .  
 $C_{17}H_{14}N_3Br$  requires  $N=12.35$  per cent.

*5-Bromo-o-tolueneazo-β-naphthylamine*,  
 $C_6H_3MeBr \cdot N_2 \cdot C_{10}H_6 \cdot NH_2$ .

This compound crystallises from methylated spirit in small, red plates melting at  $152^\circ$ :

0.1542 gave 16.6 c.c.  $N_2$  (moist) at  $15^\circ$  and 754 mm.  $N=12.52$ .  
 $C_{17}H_{14}N_3Br$  requires  $N=12.35$  per cent.

The *acetyl* derivative crystallises from ethyl acetate in orange-red, feathery needles melting at  $189^\circ$ :

0.1643 gave 0.8115 AgBr.  $Br=21.02$ .  
 $C_{19}H_{16}ON_3Br$  requires  $Br=20.94$  per cent.

The *benzoyl* derivative crystallises from ethyl acetate in pale orange, feathery needles melting at  $179^{\circ}$ :

0.1862 gave 0.7859 AgBr. Br = 17.96.

$C_{24}H_{18}ON_3Br$  requires Br = 18.02 per cent.

*2- $\beta$ -Naphthalenediazoamino-5-bromotoluene,*  
 $C_6H_3MeBr \cdot N_3H \cdot C_{10}H_7$ .

This compound crystallises from toluene in small, red needles melting at  $113^{\circ}$ . When heated with 5-bromo-*o*-toluidine and its hydrochloride at  $65^{\circ}$ , it passes into the isomeric aminoazo-compound, and when heated with  $\beta$ -naphthol it eliminates  $\beta$ -naphthylamine and yields 5-bromo-*o*-tolueneazo- $\beta$ -naphthol, which crystallises from benzene in red plates melting at  $174^{\circ}$ :

0.1459 gave 16 c.c.  $N_2$  (moist) at  $19^{\circ}$  and 749 mm. N = 12.42.

$C_{17}H_{14}N_3Br$  requires N = 12.35 per cent.

*p-Xyleneazo- $\beta$ -naphthylamine,*  $C_6H_3Me_2 \cdot N_2 \cdot C_{10}H_6 \cdot NH_2$ .

This compound crystallises from methylated spirit in brilliant orange-red needles melting at  $119^{\circ}$ :

0.1421 gave 18.6 c.c.  $N_2$  (moist) at  $17^{\circ}$  and 754 mm. N = 15.07.

$C_{18}H_{17}N_3$  requires N = 15.27 per cent.

The *acetyl* derivative crystallises from ethyl acetate in dark red needles melting at  $167^{\circ}$ :

0.1239 gave 14.2 c.c.  $N_2$  (moist) at  $15^{\circ}$  and 750 mm. N = 13.24.

$C_{20}H_{19}ON_3$  requires N = 13.25 per cent.

The *benzoyl* derivative crystallises from ethyl acetate in orange-red, feathery needles melting at  $148^{\circ}$ :

0.1761 gave 16.6 c.c.  $N_2$  (moist) at  $15^{\circ}$  and 750 mm. N = 10.9.

$C_{25}H_{21}ON_3$  requires N = 11.08 per cent.

*2- $\beta$ -Naphthalenediazoamino-p-xylene,*  $C_6H_3Me_2 \cdot N_3H \cdot C_{10}H_7$ .

This compound crystallises from benzene in brownish-red crystals melting somewhat indefinitely at  $120^{\circ}$ . On heating with *p*-xylydine and its hydrochloride, a small quantity of a yellow solid melting at  $124^{\circ}$ , and containing 11.7 per cent. of nitrogen, was obtained, but it was not further identified. On heating with  $\beta$ -naphthol, it gives  $\beta$ -naphthaleneazo- $\beta$ -naphthol and *p*-xylydine:

0.1213 gave 15.9 c.c.  $N_2$  (moist) at  $17^{\circ}$  and 754 mm. N = 15.09.

$C_{18}H_{17}N_3$  requires N = 15.27 per cent.

*3-Nitro-p-toluenediazo-β-naphthylamine,*  
 $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{NH}_2$ .

This compound crystallises from toluene in dark bronze needles melting at  $224^\circ$ :

0.1133 gave 18 c.c.  $\text{N}_2$  (moist) at  $18^\circ$  and 753 mm.  $\text{N}=18.18$ .

$\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_4$  requires  $\text{N}=18.3$  per cent.

The *acetyl* derivative crystallises from ethyl acetate or toluene in small, red needles melting at  $200^\circ$ :

0.1441 gave 20.2 c.c.  $\text{N}_2$  (moist) at  $19^\circ$  and 753 mm.  $\text{N}=15.95$ .

$\text{C}_{19}\text{H}_{16}\text{O}_3\text{N}_4$  requires  $\text{N}=16.09$  per cent.

The *benzoyl* derivative crystallises from ethyl acetate in red needles melting at  $158^\circ$ :

0.1137 gave 13.7 c.c.  $\text{N}_2$  (moist) at  $16^\circ$  and 750 mm.  $\text{N}=13.86$ .

$\text{C}_{24}\text{H}_{18}\text{O}_3\text{N}_4$  requires  $\text{N}=13.66$  per cent.

*5-Nitro-o-toluenediazo-β-naphthylamine,*  
 $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{NH}_2$ .

This compound crystallises from toluene in dark bronze needles melting at  $210^\circ$ :

0.1239 gave 19.1 c.c.  $\text{N}_2$  (moist) at  $16^\circ$  and 758 mm.  $\text{N}=17.93$ .

$\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_4$  requires  $\text{N}=18.3$  per cent.

The *acetyl* derivative crystallises from toluene in red needles melting at  $240^\circ$ :

0.1361 gave 19.2 c.c.  $\text{N}_2$  (moist) at  $17^\circ$  and 754 mm.  $\text{N}=16.24$ .

$\text{C}_{19}\text{H}_{16}\text{O}_3\text{N}_4$  requires  $\text{N}=16.09$  per cent.

The *benzoyl* derivative crystallises from toluene in red needles melting at  $197^\circ$ :

0.1356 gave 16 c.c.  $\text{N}_2$  (moist) at  $16^\circ$  and 760 mm.  $\text{N}=13.76$ .

$\text{C}_{24}\text{H}_{18}\text{O}_3\text{N}_4$  requires  $\text{N}=13.66$  per cent.

*s-Trichlorobenzediazo-β-naphthylamine,*  $\text{C}_6\text{H}_2\text{Cl}_3 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{NH}_2$ .

This compound crystallises from benzene in red needles melting at  $157^\circ$ :

0.2135 gave 0.2618 AgCl.  $\text{Cl}=30.26$ .

$\text{C}_{16}\text{H}_{10}\text{N}_3\text{Cl}_3$  requires  $\text{Cl}=30.38$  per cent.

The *acetyl* derivative crystallises from ethyl acetate in reddish-yellow needles melting at  $169^\circ$ :

0.2341 gave 0.2556 AgCl.  $\text{Cl}=27.01$ .

$\text{C}_{18}\text{H}_{12}\text{ON}_3\text{Cl}_3$  requires  $\text{Cl}=27.13$  per cent.

*Action of p-Toluidine and its Hydrochloride on Diazoamino-p-toluene in the Presence of β-Naphthylamine.*

Molecular quantities of diazoamino-*p*-toluene, *p*-toluidine hydrochloride, and β-naphthylamine were dissolved in *p*-toluidine and heated for twelve hours at 50°. On treatment with hydrochloric acid, a residue was obtained which was crystallised from methylated spirit, and melted at 112°. It was identified as *p*-tolueneazo-β-naphthylamine.

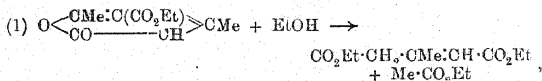
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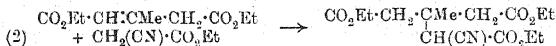
LVI.—*The Chemistry of the Glutaconic Acids.*  
*Part XI. The Occurrence of 1:3-Addition to the Normal Form.*

By JOCELYN FIELD THORPE.

IN Part IX of this series (T., 1913, 103, 1579) it was shown that the *cis*-labile ester of β-methylglutaconic acid, which can be readily formed by the action of alcoholic sodium ethoxide on ethyl *iso*-dehydracetate,



condenses with the sodium compound of ethyl cyanoacetate, giving a 60 per cent. yield of a condensation product in accordance with the equation

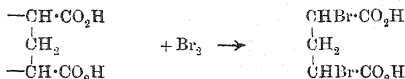


whereas the normal ester,  $\text{CO}_2\text{Et} \cdot \dot{\text{C}}\text{H} \cdot \text{CHMe} \cdot \dot{\text{C}}\text{H} \cdot \text{CO}_2\text{Et}$ , which can be prepared from the normal acid by etherification, yields no condensation product under the same experimental conditions.

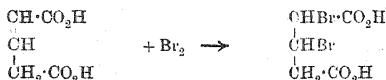
Several other esters of normal acids of the series were subjected to the same reaction, and the failure in each case to obtain a condensation product was regarded as evidence that substances possessing the normal structure which, in accordance with the

views put forward in this series, have constitutions best represented by the general formula  $\text{CO}_2\text{R}\cdot\dot{\text{C}}\text{R}\cdot\dot{\text{C}}\text{R}\cdot\text{CO}_2\text{R}$  ( $\text{R}=\text{H}$  or alkyl), do not form additive products when treated with the usual additive reagents.

The evidence is, however, negative, and during the whole course of these researches on the glutaconic acids, frequent attempts have been made to obtain direct evidence of the structure of the normal forms by inducing them to form additive products in the 1:3-positions. If, for example, bromine could be made to unite with the terminal carbon atoms of the normal system, thus:



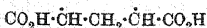
and if the isomeric compound produced from the labile modification were found to be formed in accordance with the scheme:



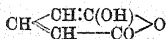
no reasonable doubt would then remain that the formulæ for the glutaconic acids suggested in this series must be a close approximation to the truth.

Unfortunately, the evidence obtained in this way is far from satisfactory. The stable normal acids of the type of  $\beta$ -methylglutaconic acid (the *cis*-acid of Feist, *Annalen*, 1906, **345**, 64, and of Fichter and Schwab, *Annalen*, 1907, **348**, 254, melting at  $149^\circ$ ) do not react with the halogen to give any definite additive products, although the *cis*-labile acid (the *trans*-acid of Feist and Fichter, melting at  $115$ — $116^\circ$ ) readily forms  $\alpha\beta$ -dibromo- $\beta$ -methylglutaric acid,  $\text{CO}_2\text{H}\cdot\text{CHBr}\cdot\text{CMeBr}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (m. p.  $145^\circ$ ), when treated with bromine in direct sunlight (Fichter and Schwab, *loc. cit.*).

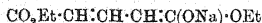
On the other hand, those acids, of which glutaconic acid itself is the best example, the labile forms of which are so unstable as to be incapable of isolation, yet readily pass, either through hydroxy-anhydride formation or through the formation of the sodium derivative of the esters, into derivatives of the labile forms (T.,



Glutaconic acid.



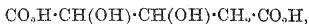
Hydroxy-anhydride.



Sodium derivative of ester.



1912, **101**, 863; 1913, **103**, 1757), react with bromine in a curious manner. For example, glutaconic acid readily absorbs the correct amount of bromine, but no one appears to have been able to isolate any definite product from the reaction mixture. Kiliani (*Ber.*, 1885, **18**, 2517) first studied the action of bromine on this acid. He noticed the rapid absorption of the halogen, but, without attempting to isolate the additive product, treated the crude reaction mixture with calcium carbonate and obtained a 10 per cent. yield of  $\alpha\beta$ -dihydroxyglutaric acid,



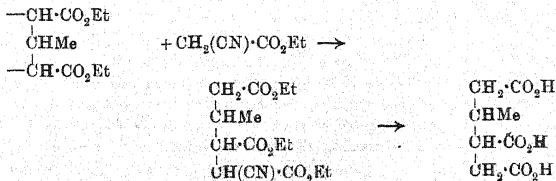
a yield which was subsequently increased to 14 per cent (*Ber.*, 1905, **38**, 3625). Ultimately, Feist (*Ber.*, 1911, **44**, 137) was able to obtain an 80—85 per cent. yield of the dibromo-ester,



by brominating ethyl glutaconate in sunlight.

It is evident, therefore, that the normal acids of this series do not react with bromine in the way one would expect an  $\alpha\beta$ -unsaturated acid to react, and that they only form additive products under conditions which favour the transformation of the normal into the labile modifications. The labile acids, on the other hand, are easily converted into  $\alpha\beta$ -dibromo-additive products in accordance with the properties of the structures assigned to them.

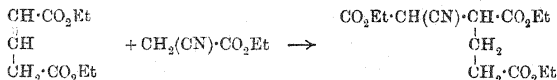
Direct evidence respecting the structure of the normal form can, however, be obtained from a study of the condensation products formed from the normal and labile esters of  $\beta$ -methylglutaconic acid with the sodium compound of ethyl cyanoacetate, for it is now found that whereas the *cis*-labile ester reacts in accordance with equation (2) and gives a yield, which has now been increased to 80 per cent., of the 1:2-additive product, the normal ester can, under special conditions described in the experimental portion, be made to yield a small quantity (approximately 6 per cent.) of a condensation product which, when hydrolysed, is converted into  $\gamma$ -methylbutane- $\alpha\beta\delta$ -tricarboxylic acid, in accordance with the scheme:



an acid which was found by direct comparison to be identical with that prepared by Hope and Perkin (T., 1911, 99, 762) by the interaction of ethyl bromoacetate and the condensation product of ethyl sodiocyanoacetate with ethyl crotonate.

There can be no question, therefore, that in this reaction addition has been effected in the 1:3-positions, and although the yield is small, the formation of a condensation product having the above composition is direct evidence of the structure of the normal form.

A similar condensation tried with ethyl glutaconate failed to bring about addition in the 1:3-positions, and the product (about 5 per cent. yield) was found to have the structure assigned to it in the previous paper (T., 1913, 103, 1580). It had therefore been formed in accordance with the scheme:



and it is evident that a small quantity of the normal ester is converted into the labile ester under the experimental conditions used. It is of interest to record at this stage a tendency that has been detected for the *cis*-labile ester to pass into the normal ester when kept. Hitherto, the *cis*-ester has been regarded as a comparatively stable substance. It distills without change, and can be hydrolysed to the corresponding *cis*-acid without conversion into the normal isomeride.

The following facts show, however, that, under certain conditions, the labile ester passes slowly into its normal form. About the middle of 1914, some 600 grams of the *cis*-labile ester had been accumulated for use in the preparation of the "enclosed" ring compound, an account of which is about to be published. It had all been prepared within the previous month, and some of it had already been used in condensation with the sodium compound of ethyl cyanoacetate, and found to give the usual yield of the condensation product. War then broke out, and the ester remaining over was laid aside until January of the present year, that is, for approximately four and a-half years. It happened that the larger quantity of the ester (about 450 grams) was placed in a deep yellow glass bottle, whereas the remaining amount (about 130 grams) was kept in a white glass bottle. Both bottles were placed side by side in a shallow cupboard with glass doors facing a strong north light. In January, 1919, the ester in the white glass bottle was noticed to have become deep brown, and when condensed with the sodium compound of ethyl cyanoacetate was found to give only 20 per

cent. of the usual condensation product. It was therefore distilled and hydrolysed, when the mixture of acids formed was found to consist of 75 per cent. of the normal acid melting at  $149^{\circ}$  and 25 per cent. of the labile acid melting at  $115$ — $116^{\circ}$ . The ester in the yellow bottle, on the other hand, was found to have altered little in colour and to give the usual yield when condensed with ethyl sodiocyanoacetate. After distillation and hydrolysis, it was found to yield the *cis*-acid melting at  $115$ — $116^{\circ}$  in an almost pure form, a small quantity, about 5 per cent. only, of the *trans*-acid being isolated. In order to check these results, a further quantity of the *cis*-labile ester was prepared from ethyl *isodehydracetate* and hydrolysed, when the product was found to be the pure *cis*-acid.

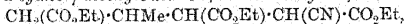
• It is evident, therefore, that exposure to light for a considerable period of time leads to the partial conversion of the *cis*-labile form into the normal modification.

#### EXPERIMENTAL.

##### *Condensation of Normal Ethyl $\beta$ -Methylglutaconate with the Sodium Compound of Ethyl Cyanoacetate.*

In the earlier attempt which was made to effect this condensation (T., 1913, 103, 1580), molecular quantities of the ingredients were used, and the mixture was heated on the water-bath for twenty-four hours. As no condensation product could be isolated under these conditions, they were altered in the present instance so as to ensure that a large excess of ethyl cyanoacetate was present throughout the reaction. Forty-two grams of the normal ester, prepared by the etherification of the normal acid, were added to an alcoholic suspension of the sodium compound of ethyl cyanoacetate prepared from 94 grams of the ester and 9.7 grams of sodium dissolved in 110 grams of alcohol, and the mixture was heated for thirty-six hours on the water-bath. Water was then added, and the acidified liquid extracted with ether. Sodium carbonate solution failed to extract any appreciable quantity of acid ester from the ethereal solution, and the latter was therefore dried and freed from ether. The residual oil was then carefully fractionated under diminished pressure, when, besides the two fractions of lower boiling point, consisting of ethyl cyanoacetate and unchanged ethyl  $\beta$ -methylglutaconate, a small fraction (about 4 grams) of high boiling point was isolated.

*Ethyl  $\alpha$ -cyano- $\gamma$ -methylbutane- $\alpha\beta$ -tricarboxylate,*



is a colourless, moderately viscid liquid which boils at  $212^{\circ}/22$  mm.:

0.1932 gave 0.4081  $\text{CO}_2$  and 0.1293  $\text{H}_2\text{O}$ .  $\text{C}=57.66$ ;  $\text{H}=7.41$ .

$\text{C}_{15}\text{H}_{23}\text{O}_6\text{N}$  requires  $\text{C}=57.5$ ;  $\text{H}=7.4$  per cent.

*$\gamma$ -Methylbutane- $\alpha\beta\delta$ -tricarboxylic Acid,*  
 $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}.$

Hope and Perkin found it necessary, in order to obtain this acid in a crystalline condition, to hydrolyse their cyano-triethyl ester to the tribasic acid, to etherify this, and, after fractionation, to isolate the potassium salt by the aid of methyl-alcoholic potassium hydroxide. Apparently there is no need to use this method in order to obtain the crystalline acid from the isomeric cyano-triethyl ester described above, because the hydrolysis proceeded rapidly and smoothly through the agency of "50 per cent." aqueous sulphuric acid. Twelve grams of the cyano-triethyl ester were dissolved in an equal volume of concentrated sulphuric acid, care being taken to keep the mixture cool, and allowed to remain at the ordinary temperature for two hours. Water was then added until the solution became slightly turbid, when it was boiled under a reflux condenser for five hours, the alcohol formed during hydrolysis being removed from time to time by detaching the condenser tube from the flask. After the cooled product had been saturated with ammonium sulphate, it was extracted with ether, and the syrupy acid, which rapidly solidified, obtained by evaporating the dried ethereal solution. The crude acid was then purified by treatment with concentrated hydrochloric acid, filtering, and recrystallising from this solvent. It melted sharply at  $154^{\circ}$  (Hope and Perkin give  $153$ — $154^{\circ}$ ) (Found:  $\text{C}=46.95$ ;  $\text{H}=6.13$ .  $\text{C}_8\text{H}_{12}\text{O}_6$  requires  $\text{C}=47.1$ ;  $\text{H}=5.9$  per cent.).

The acid was found to crystallise in nodular masses, as described by Hope and Perkin, and mixtures of it with Hope and Perkin's acid were found to have the same melting point ( $154^{\circ}$ ) as either constituent. It also gave a potassium salt insoluble in methyl-alcoholic potassium hydroxide. Unfortunately, the amount of acid available was insufficient for the purpose of preparing crystalline derivatives, because the anhydro-acid is apparently one of those intractable substances which are very difficult to obtain in a crystalline condition, similar properties being possessed by the aniline and toluidine derivatives of the anhydro-acid. All attempts to prepare these substances in a crystalline condition were

unsuccessful, and it is possible that the same difficulty was encountered by Hope and Perkin, since it will be noticed that no derivatives of this acid are described by them.

The evidence of the mixed melting point is, however, usually accepted as sufficient proof of identity. In the present instance, this is, of course, strengthened by the fact that the only other acid of this formula which could be produced in the reaction, namely,  $\beta\beta$ -dimethylpropanetricarboxylic acid,  $\text{CMe}(\text{CH}_2\cdot\text{CO}_2\text{H})_3$  (T., 1913, 103, 1583), melts at  $172^\circ$  and readily gives a crystalline anhydro-acid, which can be converted into a crystalline anil-anilide and trianilide.

*The Transformation of cis-Labile Ethyl  $\beta$ -Methylglutaconate into the Normal Form.*

There is little to add to the general description of this change given in the introductory portion. The labile ester contained in the white glass bottle, which had previously given the usual yield of the condensation product with the sodium compound of ethyl cyanoacetate, was found at the end of four and a-half years to give a yield of only 20 per cent. under the same experimental conditions. It was therefore distilled, and was found to have the same boiling point as the original ester. When hydrolysed, it was found, however, that a mixture of acids was obtained, from which an insoluble, crystalline barium salt could be isolated in large quantities when the neutral ammonium salts of the mixed acids were treated with barium chloride solution and boiled. This was collected and converted into the acid, which was found to melt at  $149^\circ$  (Found: C=49.89; H=5.68.  $\text{C}_8\text{H}_8\text{O}_4$  requires C=50.0; H=5.6 per cent.).

This acid, which was evidently, therefore, the normal acid, constituted approximately 75 per cent. of the mixture. The labile acid melting at  $115$ – $116^\circ$  was isolated in the usual manner from the mother liquors of the barium salt precipitation.

The ester which had been kept in the deep yellow bottle, and had altered little in appearance, was found on conversion into the acids to yield only a small quantity of an insoluble barium salt, from which the acid melting at  $149^\circ$  was isolated. The amount constituted about 5 per cent. of the mixed acids obtained, the remainder being the *cis*-labile acid melting at  $115$ – $116^\circ$ , which was isolated from the mother liquors. The original ester was also found to give approximately the normal yield of con-

densation product with the sodium derivative of ethyl cyanoacetate.

The change was further proved by preparing some fresh *cis*-labile ester from ethyl isodehydracetate, when the product was found to yield the pure labile acid on hydrolysis.

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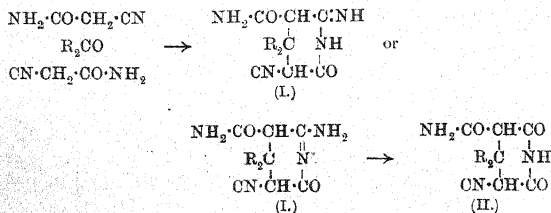
# LVII.—The Formation and Reactions of Imino-compounds. Part XIX. The Chemistry of the Cyanoacetamide and Guareschi Condensations.

By GEORGE ARMAND ROBERT KON and JOCELYN FIELD THORPE.

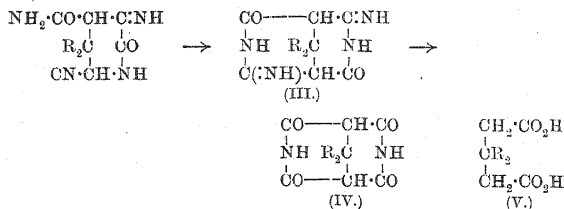
FROM the experiments described in Part XV (T., 1911, 99, 422) and Part XVIII (T., 1913, 103, 1586) of this series, it can be concluded that the condensation of cyanoacetamide with ketones in the presence of piperidine yields, to an extent of approximately 95 per cent., products which have the groups attached to the terminal carbon atoms arranged in the *trans*-positions to one another, and that approximately 5 per cent. only of the condensation product has the *cis*-configuration. The proportions vary slightly with the nature of the ketone used and with the temperature at which the condensation is carried out, but is generally of the above order when the reactions are effected at the ordinary temperature.

The following considerations support this conclusion:

(1) The chief product is obtained as a base (I) soluble in dilute mineral acid, which is quickly hydrolysed by the acid to the imide (II) in accordance with the scheme:

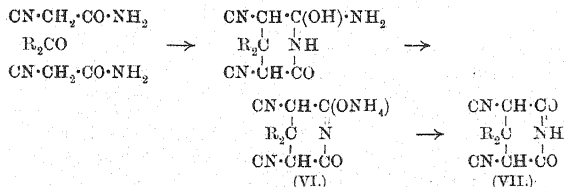


The *trans*-configuration is further proved by the formation of the di-imino-di-imide (III), thus:

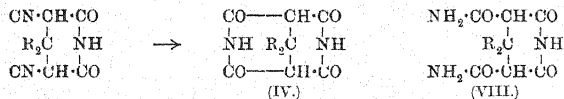


and the general structure of the whole series is shown by the production of the acid (V) from each of these compounds on complete hydrolysis.

(2) A small quantity of condensation product is also obtained which is soluble in alkali, and is evidently present in the condensation mixture as an ammonium salt (VI), since it yields the imide (VII) on treatment with mineral acids:



The *cis*-configuration of this substance follows from the production, with sulphuric acid, of a di-imide identical with (IV) or the

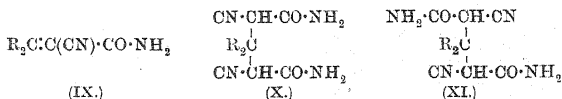


corresponding diamide (VIII), and the general structure from the fact that it yields the acid (V) on complete hydrolysis.

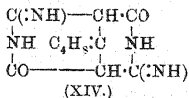
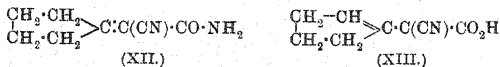
On the other hand, it is certain that when substances of these types are prepared by the action of alcoholic ammonia on a mixture of the ketone and ethyl cyanoacetate (Guareschi's method), there appears to be no tendency for the condensation product to assume the *trans*-structure, and the compounds prepared in this way have the *cis*-configuration, being, in fact, identical with the

substances of types (VI) and (VII) above. Guareschi's reactions are usually carried out at 40°, and if the cyanoacetamide condensations are effected at a similar temperature, the quantity of the *cis*-product is increased, but the fact that no trace of a *trans*-condensation product can be isolated under Guareschi's conditions shows that direction into *cis* or *trans* is dependent on the reaction and is not appreciably affected by the temperature.

It is evident that the cyanoacetamide condensation can also yield three other products, namely, the initial condensation product (IX) and the open-chain compounds (X) and (XI), and that the isolation of these substances must depend (1) on the



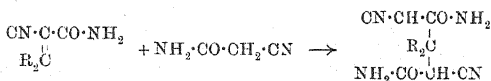
tendency for the double compound to form, and (2) on the tendency which exists for the six-membered ring to be produced. As regards (X) and (XI), we have not been able to isolate any trace of them in ketone condensations, although, as will be shown in a subsequent paper, they are the chief products when certain aldehydes are used in place of ketones. The formation of (IX) has been noticed in one case, which is described in this paper, and its production and reactions clearly show the general mechanism of these condensations. It was found, for example, that when *cyclopentanone* is condensed with cyanoacetamide under conditions which usually yield the cyclic imino-compound (type I), the product is the unsaturated amide (XII).



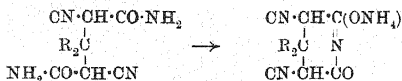
It is true that this amide yields, on treatment with nitrous acid,  $\alpha$ -cyano- $\Delta^1$ -cyclopenteneacetic acid (XIII), identical with the compound obtained by Harding and Haworth (T., 1910, 97, 486), but the fact that it readily condenses with more cyanoacetamide to form the di-imino-compound (XIV) is, we think, proof that it must have the formula (XII). Its precipitation in the present instance is due entirely to its insolubility in the aqueous medium



used, because, if sufficient alcohol is employed, the reaction pursues a normal course with the direct production of the di-imino-derivative (XIV). The production of this intermediate product is, however, of interest, since it is probable that in all cases of this kind the initial condensation leads to the formation of the unsaturated derivative, which then reacts further with cyanoacetamide, forming the glutaric derivative. If this is the correct explanation, it is easy to understand the difference between the cyanoacetamide condensation and the Guareschi reaction, because, in the former case, it is to be anticipated that the addition of cyanoacetamide will lead to the more stable *trans*-configuration,



whereas in Guareschi's reaction the presence of excess of ammonia causes the production of the *cis*-derivative, owing to the tendency for the compound to pass into the ammonium salt,

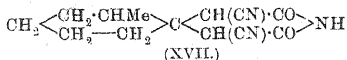
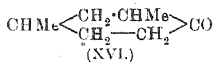
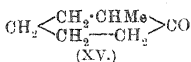


The latter is therefore an "enforced" reaction, and can, as will be shown, be made to yield condensation products in cases where a true catalytic reaction, such as the cyanoacetamide reaction, fails owing to a lack of tendency on the part of the ketone to yield a condensation product. It is found, for example, that the cyanoacetamide reaction can be effected with all ketones having two secondary carbon atoms next to the carbonyl group. If one of these is tertiary, the cyanoacetamide condensation fails, but products can be obtained by the Guareschi method, although in diminished yield. If both carbon atoms are tertiary, both the cyanoacetamide reaction and Guareschi's reaction fail to yield condensation products, and the same is the case if one carbon atom is quaternary, as in camphor and pinacolin.

We have been led to adopt this explanation of the course of the two reactions on account of the results of a series of experiments which have now been carried out on the question of the elimination of an alkyl group from the ortho-position during the condensation of ketones containing such groups with cyanoacetamide.

In Part XVIII (*loc. cit.*) it was noticed that 2-methylcyclohexanone (XV) and 2:4-dimethylcyclohexanone (XVI) gave with cyanoacetamide and piperidine the same condensation products as

those derived from *cyclohexanone* and 4-methyl*cyclohexanone* respectively:



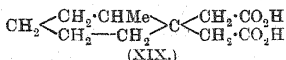
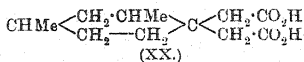
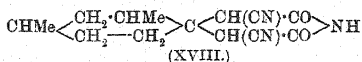
Great care was taken to purify these ketones, and although the yields of the condensation products were small and the reactions very sluggish, their constitutions were unquestionable. It was therefore assumed that the inhibiting effect of the ortho-methyl group prevented condensation, but that a certain portion of the ketone eliminated the inhibiting methyl group and yielded the product next lower in the series. At the same time, it was mentioned that Squintani (*Atti R. Accad. Sci. Torino*, 1912—1913, 48, 675) had prepared from 2-methyl*cyclohexanone* by the Guareschi method a condensation product melting at 210°, to which he assigned the structure XVI. It was also pointed out that the melting point of this substance was very close to that of the corresponding compound from *cyclohexanone*, namely, 211—212°, and it was suggested that in this case also the ortho-methyl group had been eliminated.

The whole question has now been re-examined, and the pure *o*-methyl ketones have been regenerated from the carefully purified semicarbazones, with the result that it has been established beyond question that the ortho-substituted ketones do not react with cyanoacetamide, but give by the Guareschi method a poor yield of the ortho-substituted condensation product.

It follows also that the "pure" *o*-methyl ketones of Messrs. Poulenc contain appreciable quantities of the next lower homologue, which, curiously enough, cannot be detected either by analysis or by the precipitation of the semicarbazones, a fact that can be demonstrated in the following way. The "pure" 2-methyl*cyclohexanone* of Messrs. Poulenc when treated with semicarbazide in slight excess was found to give a semicarbazone melting at 183—184°, in the crude condition, and at 190—191°, the correct melting point of the semicarbazone of 2-methyl*cyclohexanone*, after being once recrystallised from alcohol (the semicarbazone of *cyclohexanone* melts at 163°). A mixture of pure *cyclohexanone* (15 per cent.) and pure 2-methyl*cyclohexanone* (85 per cent.) was then made up, when it was found that a semicarbazone of the same melting point (183—184°) as that derived from the Poulenc

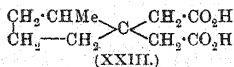
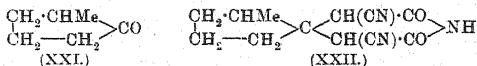
ketone was obtained. As a matter of fact, the presence of *cyclohexanone* could not be detected at all in this mixture. In the same way, the pure semicarbazone of 2:4-dimethyl*cyclohexanone* (melting at 194°) was precipitated from the "pure" ketone of Messrs. Poulenc, although the presence in it of at least 10 per cent. of 4-methyl*cyclohexanone* is clearly indicated by the experiments described in this paper.

Messrs. Poulenc informed us that this ketone must be free from 4-*cyclohexanone*, because it is prepared by the Sabatier-Senderens process from *m*-4-xlenol. It is evident, however, that the ortho-methyl group is eliminated during the Sabatier-Senderens reduction, and not during the cyanoacetamide condensation. It is also evident that Squintani was dealing with a similar mixture of *cyclohexanone* and 2-methyl*cyclohexanone*, since the condensation product (XVII) prepared from the pure ortho-methyl ketone melts at 245°, and not at 210°. The structures of our products (XVII) and (XVIII) follows from the fact that they are completely converted into the acids (XIX) and (XX) on complete hydrolysis.

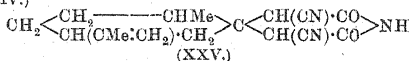
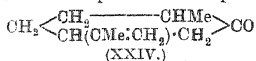


In order still further to emphasise the difference between the two types of reactions, we have investigated several other ketones having one tertiary carbon atom next to the carbonyl group. These compounds do not form condensation products with cyanoacetamide, but condense to a limited extent (the yield is usually about 15—20 per cent.) when subjected to the Guareschi reaction. These results may be summarised as follows.

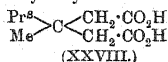
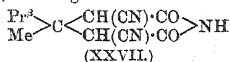
2-Methyl*cyclopentanone* (XXI) yields the condensation product (XXII), which is transformed into the acid (XXIII) on hydrolysis:



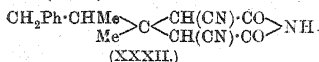
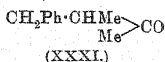
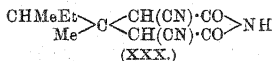
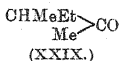
Dihydrocarvone (XXIV) gives a fairly good yield of the condensation product (XXV), which, however, cannot be hydrolysed without deep-seated decomposition.



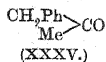
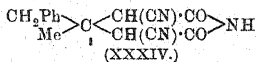
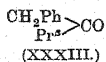
Methyl *isopropyl* ketone (XXVI) leads to the condensation product XXVII, which gives the acid XXVIII on hydrolysis:



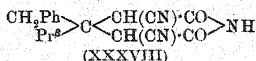
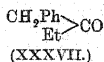
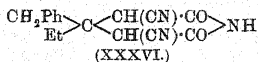
Methyl *ψ*-butyl ketone (XXIX) is converted into the product XXX, and benzylethyl methyl ketone (XXXI) into the compound XXXII:



The condensation of benzyl *isopropyl* ketone (XXXIII) with ethyl cyanoacetate and alcoholic ammonia has been described by Guareschi (*Gazzetta*, 1918, 48, 97), who obtained a condensation product melting at 248°. We have repeated this condensation with the ketone supplied by Messrs. Poulenc, and have isolated both Guareschi's compound and also another which melts at 214—216°. The former we have identified as the benzylmethyl derivative (XXXIV) which we prepared from benzyl methyl ketone (XXXV):



The latter was found to be identical with the benzylethyl derivative (XXXVI) prepared in a similar manner from pure benzyl ethyl ketone (XXXVII):



It is evident, therefore, that the benzyl *isopropyl* ketone used by Guareschi and by us contained considerable quantities of benzyl ethyl and benzyl methyl ketones. In order to settle this point, we prepared the pure benzyl *isopropyl* ketone by distilling a mixture of the calcium salts of phenylacetic and *isobutyric* acids in accordance with Ludlam's method (T., 1902, **81**, 1185). The purity of the ketone was controlled by the formation of the semicarbazone, which we found to melt at 138—139°, in agreement with the figure found by Blaise (*Compt. rend.*, 1901, **132**, 480), and not at 126°, the number given by Senderens (*Compt. rend.*, 1910, **150**, 1138).

When condensed with ethyl cyanoacetate by the Guareschi method, no trace of the condensation product (XXXVIII) could be isolated, and it would appear, therefore, that the occurrence of these lower homologues in commercial benzyl *isopropyl* ketone is another example of the elimination of ortho-alkyl groups.

Some of the acids formed from these condensation products on hydrolysis appear to be abnormal, and a description of them is therefore reserved for a future communication.

#### EXPERIMENTAL.

The condensation of ketones with cyanoacetamide was carried out in the manner already described (T., 1911, **99**, 424). For the condensations with ethyl cyanoacetate, Guareschi's instructions were, in the main, followed. The ketone (one molecular proportion) was mixed with ethyl cyanoacetate (two molecular proportions), and a little more than three molecular proportions of ammonia, dissolved in absolute methyl or ethyl alcohol, added to the mixture. The solution assumed a yellow or orange colour and became warm. It was kept at 40° for forty-eight hours, by which time the ammonium salt of the dicyanopiperidine derivative had separated; in many instances, some cyanoacetamide was precipitated at the same time. In all cases, sufficient water was added to dissolve the salt, the solution extracted with ether to remove unchanged ketone, and the extracted solution acidified, when the dicyanopiperidine was precipitated, usually in several crops. All the compounds of this type were found to be colourless and to crystallise remarkably well.

#### *2-Methylcyclohexanone* (XV, p. 690).

This ketone, when carefully purified by regeneration it from the pure semicarbazone, does not condense with cyanoacetamide, the latter being recovered unchanged.

With ethyl cyanoacetate and alcoholic ammonia, the commercial preparations of the ketone give mixtures containing varying quantities of two compounds, one melting at 207° and the other at 245°. They can be separated by a tedious process of fractional crystallisation from 50 per cent. aqueous alcohol; the compound of higher melting point is the less soluble and crystallises out first, but mixtures of various melting points, ranging from 190° to 210°, are obtained intermediately, and this probably accounts for the results obtained by Squintani (see p. 690).

The compound melting at 207° was identified by direct comparison and by analysis (Found: C=62.28; H=5.79.  $C_{12}H_{13}O_2N_3$  requires C=62.3; H=5.6 per cent.) as the  $\omega$ -imide of  $\alpha\alpha'$ -dicyanocyclohexane-1:1-diacetic acid,  $C_5H_{10}:C \begin{smallmatrix} \text{CH(CN) \cdot CO} \\ \text{CH(CN) \cdot CO} \end{smallmatrix} NH$  (compare Thorpe and Wood, T., 1913, 103, 1592). On hydrolysis with 60 per cent. sulphuric acid, it yielded cyclohexane-1:1-diacetic acid, melting at 181°, which was identified by direct comparison with a specimen prepared from cyclohexanone.

The compound melting at 245° is the sole product of the reaction if the ketone used is absolutely pure; the yield is about 3 grams from 11.2 grams of the ketone.

The  $\omega$ -imide of  $\alpha\alpha'$ -dicyano-2-methylcyclohexane-1:1-diacetic acid (XVII, p. 690) crystallises from 50 per cent. aqueous alcohol in glistening plates and melts at 245° with slight decomposition:

0.1016 gave 0.2375  $CO_2$  and 0.0557  $H_2O$ . C=63.80; H=6.09.

0.1182 „ 17.7 c.c.  $N_2$  at 19° and 766 mm. N=17.34.

$C_{13}H_{15}O_2N_3$  requires C=63.7; H=6.1; N=17.1 per cent.

The  $\omega$ -imide of  $\alpha\alpha'$ -dicarbamyl-2-methylcyclohexane-1:1-diacetic acid,  $CH_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} C \begin{smallmatrix} \text{CH(CO \cdot NH}_2 \text{) \cdot CO} \\ \text{CH(CO \cdot NH}_2 \text{) \cdot CO} \end{smallmatrix} NH$ , is obtained as a microcrystalline precipitate when the above dicyano-derivative is dissolved in ten times its weight of concentrated sulphuric acid and the solution, after keeping for twenty-four hours at the ordinary temperature, is poured into ice-water. It crystallises from absolute alcohol in small plates, which melt and decompose at 275°:

0.1357 gave 0.2735  $CO_2$  and 0.0828  $H_2O$ . C=54.96; H=6.78.

0.1583 „ 21 c.c.  $N_2$  at 21° and 755 mm. N=14.94.

$C_{18}H_{19}O_4N_3$  requires C=55.5; H=6.8; N=14.9 per cent.

2-Methylcyclohexane-1:1-diacetic acid (XIX, p. 691) is formed in excellent yield when the dicyano-derivative is hydrolysed by 60 per cent. sulphuric acid in accordance with the method described by Thole and Thorpe (T., 1911, 99, 434). It crystallises from dilute alcohol in colourless, iridescent plates, or from benzene,

in which it is sparingly soluble, in prismatic needles. Both forms melt at  $148^{\circ}$ :

0.1088 gave 0.2462  $\text{CO}_2$  and 0.0816  $\text{H}_2\text{O}$ .  $\text{C}=61.70$ ;  $\text{H}=8.33$ .

$\text{C}_{11}\text{H}_{15}\text{O}_4$  requires  $\text{C}=61.7$ ;  $\text{H}=8.4$  per cent.

A normal solution of the neutral ammonium salt of the acid does not give a precipitate with either barium or calcium chlorides, but if more concentrated solutions are used, a copious precipitate of the calcium salt can be obtained on boiling. The *silver* salt is a white, curdy precipitate:

0.1266 gave 0.0634 Ag.  $\text{Ag}=50.05$ .

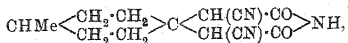
$\text{C}_{11}\text{H}_{15}\text{O}_4\text{Ag}_2$  requires  $\text{Ag}=50.45$  per cent.

Neither the anhydride nor the semianilide of this acid could be obtained in a crystalline condition, although the former can be readily prepared as an oil, insoluble in aqueous sodium hydrogen carbonate solution, by treating the acid with hot acetyl chloride.

#### 2:4-Dimethylcyclohexanone (XVI, p. 690).

The pure ketone, regenerated from the semicarbazone, does not condense with cyanoacetamide. Commercial preparations of the ketone readily condense with ethyl cyanoacetate, 12.6 grams of the ketone giving about 3.2 grams of a crude condensation product melting at  $205-210^{\circ}$ .

On recrystallisation from alcohol, a small amount of a substance crystallising in needles and melting at  $213^{\circ}$  is obtained from the more soluble portion. This substance was identified as the  $\omega$ -imide of *aa'*-dicyano-4-methylcyclohexane-1:1-diacetic acid,



by direct comparison with a specimen prepared from 4-methylcyclohexanone. The bulk of the product consists of the  $\omega$ -imide of *aa'*-dicyano-2:4-dimethylcyclohexane-1:1-diacetic acid (XVIII, p. 691), which crystallises from alcohol in sparkling plates melting at  $236^{\circ}$ , not unlike the 2-methyl compound in appearance:

0.1254 gave 0.2970  $\text{CO}_2$  and 0.0751  $\text{H}_2\text{O}$ .  $\text{C}=64.60$ ;  $\text{H}=6.65$ .

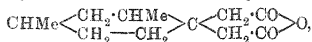
$\text{C}_{14}\text{H}_{17}\text{O}_2\text{N}_3$  requires  $\text{C}=64.9$ ;  $\text{H}=6.6$  per cent.

2:4-Dimethylcyclohexane-1:1-diacetic acid (XX, p. 691) is obtained in good yield when the above dicyano-imide is hydrolysed with 60 per cent. sulphuric acid. It crystallises from water containing a little alcohol in long, prismatic needles melting at  $152^{\circ}$ , and is very sparingly soluble in benzene:

0.1180 gave 0.2730  $\text{CO}_2$  and 0.0935  $\text{H}_2\text{O}$ .  $\text{C}=63.10$ ;  $\text{H}=8.80$ .

$\text{C}_{12}\text{H}_{20}\text{O}_4$  requires  $\text{C}=63.2$ ;  $\text{H}=8.8$  per cent.

2:4-Dimethylcyclohexane-1:1-diacetic anhydride,



which can be obtained by boiling the acid with acetyl chloride, crystallises from light petroleum (b. p.  $60-80^\circ$ ), containing a little benzene, in colourless plates melting at  $68.5^\circ$ :

0.1173 gave 0.2959  $\text{CO}_2$  and 0.0918  $\text{H}_2\text{O}$ .  $\text{C}=68.77$ ;  $\text{H}=8.70$ .

$\text{C}_{12}\text{H}_{18}\text{O}_3$  requires  $\text{C}=68.6$ ;  $\text{H}=8.6$  per cent.

The *semianilide*, prepared in the usual manner from a benzene solution of the anhydride and aniline, crystallises from dilute alcohol in glistening laminae melting at  $151^\circ$ :

0.1095 gave 0.2850  $\text{CO}_2$  and 0.0820  $\text{H}_2\text{O}$ .  $\text{C}=70.97$ ;  $\text{H}=8.13$ .

$\text{C}_{18}\text{H}_{23}\text{O}_3\text{N}$  requires  $\text{C}=71.3$ ;  $\text{H}=8.3$  per cent.

#### *Dihydrocarvone* (XXIV, p. 692).

The ketone was prepared by the reduction of carvone by zinc dust and sodium hydroxide (Wallach, *Annalen*, 1894, **279**, 377). It does not combine with cyanoacetamide, but condenses fairly readily with ethyl cyanoacetate, the yield of condensation product being about 3 grams from 15.2 grams of the ketone. Care should be taken to remove the unchanged ketone by repeated extraction with ether, otherwise the condensation product is difficult to purify. The sole product of the reaction is the *ω-imide* of *αα'-dicyano-2-methyl-5-isopropylidenecyclohexane-1:1-diacetic acid* (XXV, p. 692), which separates from dilute alcohol in clusters of silky needles melting at  $198-199^\circ$ , but sintering and darkening at  $197^\circ$ :

0.1091 gave 0.2698  $\text{CO}_2$  and 0.0667  $\text{H}_2\text{O}$ .  $\text{C}=67.61$ ;  $\text{H}=6.79$ .

0.1131 „ 0.2782  $\text{CO}_2$  „ 0.0688  $\text{H}_2\text{O}$ .  $\text{C}=67.05$ ;  $\text{H}=6.76$ .

0.0860 „ 10.8 c.c.  $\text{N}_2$  at  $14.5^\circ$  and 774.5 mm.  $\text{N}=15.00$ .

$\text{C}_{16}\text{H}_{19}\text{O}_2\text{N}_3$  requires  $\text{C}=67.4$ ;  $\text{H}=6.7$ ;  $\text{N}=14.7$  per cent.

Several attempts were made to hydrolyse this compound to the corresponding non-nitrogenous acid, but a deep-seated decomposition appeared to take place, and we were unable to isolate any crystalline product.

#### *2-Methylcyclopentanone* (XXI, p. 691).

This compound was prepared by the hydrolysis of the corresponding carboxylic ester with dilute sulphuric acid, according to



Dieckmann's method (*Annalen*, 1901, **317**, 27). It does not combine with cyanoacetamide, and only gives a very poor yield of condensation product with ethyl cyanoacetate. This consists of the  $\omega$ -imide of  $\alpha\alpha'$ -dicyano-2-methylcyclopentane-1:1-diacetic acid (XXII, p. 691), which crystallises from alcohol in glistening plates melting at  $237^{\circ}$ :

0.0943 gave 0.2109  $\text{CO}_2$  and 0.0484  $\text{H}_2\text{O}$ .  $\text{C}=62.40$ ;  $\text{H}=5.70$ .

$\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}_2$  requires  $\text{C}=62.3$ ;  $\text{H}=5.6$  per cent.

2-Methylcyclopentane-1:1-diacetic acid (XXIII, p. 691) is obtained from the above dicyano-imide on hydrolysing it with 60 per cent. aqueous sulphuric acid. It crystallises from a mixture of benzene and light petroleum (b. p.  $60$ — $80^{\circ}$ ) in small prisms melting at  $112^{\circ}$ :

0.1361 gave 0.3010  $\text{CO}_2$  and 0.0998  $\text{H}_2\text{O}$ .  $\text{C}=60.33$ ;  $\text{H}=8.15$ .

$\text{C}_{10}\text{H}_{16}\text{O}_4$  requires  $\text{C}=60.0$ ;  $\text{H}=8.0$  per cent.

#### *cycloPentanone.*

The greater part of the ketone required was prepared by distilling adipic acid with a small quantity of baryta (D.R.-P., Appl. F.33624). The method gives a yield far superior to that obtained by the dry distillation of calcium adipate or by Blanc's method involving the use of acetic anhydride.

*Condensation with Cyanoacetamide.*—*cycloPentanone* reacts in this condensation differently from *cyclohexanone* and its derivatives, owing, presumably, to the greater solubility of the normal condensation product. If the operation is carried out at the ordinary temperature, very little of the imino-compound is formed even if an excess of cyanoacetamide is used. The main product is the amide of  $\alpha$ -cyano- $\Delta^1$ -cyclopenteneacetic acid (XII, p. 688), which separates in several crops, usually in rhombohedral crystals. The yield is about 6 grams from 25 grams of cyanoacetamide. A little imino-compound (melting at  $287^{\circ}$ , see p. 688) also separates in the later stages, and on acidifying the mother liquor, some diimide (see p. 688) is obtained. The amide possesses a remarkable tendency to crystallise, and can be recrystallised from almost any of the usual solvents. It separates from water in magnificent, long needles, closely resembling phthalic anhydride in appearance. From alcohol, in which it is freely soluble, rhombohedral aggregates are obtained. Similar crystals separate from ethyl acetate, whereas from chloroform, benzene, or light petroleum the compound crystallises in needles. It melts at  $134^{\circ}$ :

0.1257 gave 0.2949  $\text{CO}_2$  and 0.0756  $\text{H}_2\text{O}$ .  $\text{C}=63.98$ ;  $\text{H}=6.68$ .

0.1318 „ 21.5 c.c.  $\text{N}_2$  at  $13^\circ$  and 755.5 mm.  $\text{N}=18.93$ .

$\text{C}_8\text{H}_{10}\text{ON}_2$  requires  $\text{C}=64.0$ ;  $\text{H}=6.7$ ;  $\text{N}=18.7$  per cent.

On prolonged boiling with water, and especially dilute alkali, ammonia and some *cyclopentanone* are evolved. On acidifying and extracting with ether, an acid is obtained melting at  $130\text{--}131^\circ$ . This acid is, however, more conveniently prepared by dissolving the amide (1 gram) in concentrated sulphuric acid (5 c.c.) and slowly adding 6 c.c. of a 20 per cent. sodium nitrite solution to the ice-cold mixture, the reaction being completed by warming on the water-bath for half an hour. On cooling, the solution deposits the acid in thin, felted needles, which, after recrystallisation from a mixture of benzene and light petroleum, melt at  $130\text{--}131^\circ$  (Found:  $\text{C}=63.70$ ;  $\text{H}=6.18$ ;  $\text{N}=9.57$ .  $\text{C}_8\text{H}_9\text{O}_2\text{N}$  requires  $\text{C}=63.6$ ;  $\text{H}=6.0$ ;  $\text{N}=9.3$  per cent.). The acid is evidently identical with  $\alpha$ -cyano- $\Delta^1$ -*cyclopenteneacetic acid* (XII, p. 688) obtained by Harding and Haworth (T., 1910, 97, 486).

If the condensation of *cyclopentanone* with cyanoacetamide is effected at a higher temperature and care is taken to prevent the precipitation of the amide by adding more alcohol, the reaction proceeds a step further. Thus when 14 grams of cyanoacetamide are dissolved in 50 c.c. of water, 7 c.c. of *cyclopentanone*, 50 c.c. of alcohol, and a few drops of piperidine added, the liquid, after being kept for some time at  $37^\circ$ , deposits a microcrystalline solid, melting and decomposing at  $287^\circ$ , which is completely soluble in dilute mineral acids, and appears to be the  $\omega$ -di-iminodi-imide of *cyclopentane-1:1-dimalonic acid* (XIV, p. 688). The yield of this substance is, however, poor, and the condensation is not to be recommended for the preparation of the corresponding diacetic acid. Much of the imino-compound remains in solution, and separates on acidifying as the di-imide (see below). The formation of the acid by-product (the dicyano-imide) was not observed.

A similar result is obtained when an alcoholic solution of cyanoacetamide (one molecule) and the amide of  $\alpha$ -cyano- $\Delta^1$ -*cyclopenteneacetic acid* (p. 688) is mixed with a few drops of piperidine and allowed to remain at  $40^\circ$ . A small amount of the imino-compound (XIV, p. 688) is deposited first, and, on acidifying, the di-imide separates.

The di-iminodi-imide (XIV, p. 688) is soluble in dilute mineral acids, and separates again if the solution is immediately poured into aqueous sodium acetate, but even then a partial hydrolysis of the imino-groups occurs, and concordant figures could not be obtained on analysis. For the same reason, the platinichloride could not be prepared uncontaminated with ammonium platin-

chloride. The specimen for analysis was therefore purified by washing, and the analytical figures lead to the formula  $C_{11}H_{14}O_2N_4 + \frac{1}{2}H_2O$ , but it must be remembered that the compounds of this type burn only with the greatest difficulty:

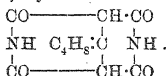
0.1590 gave 0.3177  $CO_2$  and 0.0920  $H_2O$ .  $C=54.50$ ;  $H=6.43$ .

0.1125 „ 0.2255  $CO_2$  „ 0.0647  $H_2O$ .  $C=54.67$ ;  $H=6.39$ .

0.1535 „ 29.8 c.c.  $N_2$  at  $8.5^\circ$  and 760 mm.  $N=23.36$ .

$C_{11}H_{14}O_2N_4 + \frac{1}{2}H_2O$  requires  $C=54.3$ ;  $H=6.2$ ;  $N=23.1$  per cent.

*The  $\omega$ -Di-imide of cyclopentane-1:1-dimalonic Acid,*



This compound is obtained on acidifying the mother liquors from which the di-imino-compound has been filtered off, or by boiling the latter with dilute hydrochloric acid for a short time. It can be produced in a variety of crystalline forms—usually in fern-shaped aggregates of prisms—if allowed to separate slowly from the original liquors. When recrystallised from much alcohol or glacial acetic acid, it is obtained in small, silvery plates which decompose without melting at about  $360^\circ$ :

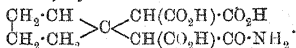
0.1282 gave 0.2608  $CO_2$  and 0.0616  $H_2O$ .  $C=55.48$ ;  $H=5.34$ .

0.1814 „ 18.2 c.c.  $N_2$  at  $8^\circ$  and 757 mm.  $N=12.03$ .

$C_{11}H_{12}O_4N_2$  requires  $C=55.9$ ;  $H=5.1$ ;  $N=11.9$  per cent.

The di-imide slowly dissolves in sodium carbonate solution, but is sparingly soluble in all organic solvents.

*The Amide of cyclopentane-1:1-dimalonic Acid,*



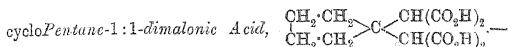
When either the above di-imide or the dicyano-imide (see below) is boiled with a slight excess of 20 per cent. aqueous potassium hydroxide for not longer than three-quarters of an hour, the solution deposits this amido-acid as a crystalline precipitate when acidified. It can be recrystallised from water, and melts with vigorous decomposition at  $157^\circ$ :

0.1636 gave 0.2907  $CO_2$  and 0.0819  $H_2O$ .  $C=48.46$ ;  $H=5.56$ .

$C_{11}H_{17}O_7N$  requires  $C=48.4$ ;  $H=5.5$  per cent.

0.1647 required 18.20 c.c. of  $N/10$ -NaOH for neutralisation.

$C_{11}H_{17}O_7N$  (tribasic) requires 18.10 c.c.

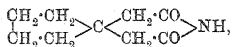


When a solution of the above amido-acid in an excess of 10 per cent. sodium hydroxide solution is boiled until no more ammonia is evolved, and the solution is acidified, the above acid separates. It crystallises from hydrochloric acid in plates, which decompose at 169° into carbon dioxide and cyclopentane-1:1-diacetic acid:

0.1062 gave 0.1872 CO<sub>2</sub> and 0.0510 H<sub>2</sub>O. C=48.10; H=5.34.

C<sub>11</sub>H<sub>14</sub>O<sub>3</sub> requires C=48.2; H=5.1 per cent.

The imide of cyclopentane-1:1-diacetic acid,

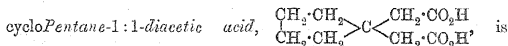


is prepared by heating the amido-tricarboxylic acid at a temperature a few degrees above its melting point until the evolution of carbon dioxide has ceased. It crystallises from water in glistening plates melting at 153°:

0.1139 gave 0.2705 CO<sub>2</sub> and 0.0805 H<sub>2</sub>O. C=64.77; H=7.85.

0.1652 „ 13.0 c.c. N<sub>2</sub> at 26.5° and 760.3 mm. N=8.68.

C<sub>9</sub>H<sub>13</sub>O<sub>2</sub>N requires C=64.7; H=7.8; N=8.4 per cent.



obtained in excellent yield when either the imino-compound or the di-imide are hydrolysed with sulphuric acid in the usual way. The acid crystallises from water in fern-shaped aggregates of prismatic needles melting at 176—177°. It is sparingly soluble in benzene:

0.1371 gave 0.2910 CO<sub>2</sub> and 0.0920 H<sub>2</sub>O. C=57.89; H=7.46.

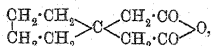
C<sub>9</sub>H<sub>14</sub>O<sub>4</sub> requires C=58.1; H=7.5 per cent.

A normal solution of the neutral ammonium salt of the acid gives no precipitate with barium chloride either in the cold or on boiling. On boiling with normal calcium chloride solution, a white precipitate is formed, which does not redissolve on cooling. The silver salt is a white, curdy precipitate, which slowly darkens on exposure to light:

0.2149 gave 0.1159 Ag. Ag=53.84.

C<sub>9</sub>H<sub>12</sub>O<sub>4</sub>Ag<sub>2</sub> requires Ag=54.0 per cent.

cycloPentane-1:1-diacetic anhydride,



is obtained when the acid is boiled with an excess of acetic anhydride or acetyl chloride, and crystallises as the reagent

evaporates. It separates from light petroleum (b. p. 60—80°) containing a little benzene in iridescent laminae melting at 68°:

0.1528 gave 0.3586 CO<sub>2</sub> and 0.0936 H<sub>2</sub>O. C=64.02; H=6.81.

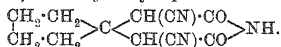
C<sub>9</sub>H<sub>12</sub>O<sub>3</sub> requires C=64.3; H=7.0 per cent.

The *semiamilide* is readily obtained on boiling the anhydride and aniline in benzene solution. It crystallises from alcohol in large, colourless laminae melting at 118°:

0.1127 gave 0.2852 CO<sub>2</sub> and 0.0730 H<sub>2</sub>O. C=69.03; H=7.20.

C<sub>15</sub>H<sub>19</sub>O<sub>3</sub>N requires C=69.0; H=7.3 per cent.

*The ω-Imide of αα'-Dicyanocyclopentane-1:1-diacetic Acid,*



This compound is obtained when *cyclopentanone* is condensed with ethyl cyanoacetate in the presence of alcoholic ammonia, the yield being about 50 per cent. of the theoretical. As a good yield of *cyclopentane-1:1-diacetic acid* can be easily obtained from the dicyano-imide on hydrolysis, this condensation is the best means for preparing the acid in quantity. The imide crystallises from dilute alcohol in stellate clusters of needles melting at 179—180°:

0.1588 gave 0.3531 CO<sub>2</sub> and 0.0717 H<sub>2</sub>O. C=60.63; H=5.02.

C<sub>11</sub>H<sub>11</sub>O<sub>2</sub>N<sub>2</sub> requires C=60.8; H=5.1 per cent.

The *ω-imide of αα'-dicarbamylecyclopentane-1:1-diacetic acid*, C<sub>4</sub>H<sub>8</sub>:C  $\begin{array}{l} \text{CH}(\text{CO}\cdot\text{NH}_2)\cdot\text{CO} \\ \text{CH}(\text{CO}\cdot\text{NH}_2)\cdot\text{CO} \end{array}$  NH, is formed from the dicyano-derivative when it is treated with cold, concentrated sulphuric acid. It crystallises from much alcohol in small, colourless prisms, which darken at 285° and carbonise without melting at 310°:

0.1166 gave 0.2219 CO<sub>2</sub> and 0.0631 H<sub>2</sub>O. C=51.88; H=6.01.

0.1620 „ 23.4 c.c. N<sub>2</sub> at 15.5° and 751.5. N=16.62.

C<sub>11</sub>H<sub>15</sub>O<sub>4</sub>N<sub>3</sub> requires C=52.2; H=5.9; N=16.6 per cent.

Complete hydrolysis of the above compounds with 60 per cent. sulphuric acid leads to *cyclopentane-1:1-diacetic acid*.

#### *Methyl isoPropyl Ketone* (XXVI, p. 692).

This ketone does not condense with cyanoacetamide. The condensation with ethyl cyanoacetate has already been carried out by Guareschi (*Atti R. Accad. Sci. Torino*, 1901, 50, 288), but he did not analyse the product.

We find that 8.6 grams of the ketone when treated with 22.6

grams of ethyl cyanoacetate and 50 c.c. of alcoholic ammonia (12 per cent.) give 3.2 grams of the condensation product, which is the *ω*-imide of *αα'*-dicyano-*β*-methyl-*β*-isopropylglutaric acid (XXVII, p. 692). It crystallises from alcohol in lustrous plates which melt at 233—234°:

0.1271 gave 0.2815 CO<sub>2</sub> and 0.0656 H<sub>2</sub>O. C=60.40; H=5.74.

0.1603 „ 26.1 c.c. N<sub>2</sub> at 9° and 756 mm. N=19.40.

C<sub>11</sub>H<sub>13</sub>O<sub>2</sub>N<sub>3</sub> requires C=60.3; H=5.9; N=19.2 per cent.

*β*-Methyl-*β*-isopropylglutaric acid (XXVIII, p. 692) is produced when the above imide is hydrolysed with 60 per cent. sulphuric acid. It crystallises from benzene in small plates melting at 100°:

0.1315 gave 0.2761 CO<sub>2</sub> and 0.0994 H<sub>2</sub>O. C=57.26; H=8.40.

C<sub>9</sub>H<sub>16</sub>O<sub>4</sub> requires C=57.4; H=8.5 per cent.

*β*-Methyl-*β*-isopropylglutaric anhydride,  $\begin{matrix} \text{Pr}^s \\ \text{Me} \end{matrix} > \text{C} < \begin{matrix} \text{CH}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CO} \end{matrix} > \text{O}$ ,

is prepared by boiling the acid for a short time with acetyl chloride. It crystallises from light petroleum (b. p. 60—80°) mixed with a small quantity of the same solvent boiling at 80—100° in glistening plates melting at 41—42°:

0.1181 gave 0.2740 CO<sub>2</sub> and 0.0880 H<sub>2</sub>O. C=63.28; H=8.28.

C<sub>9</sub>H<sub>14</sub>O<sub>3</sub> requires C=63.5; H=8.2 per cent.

#### *Methyl ψ-Butyl Ketone* (XXIX, p. 692).

This ketone was prepared by the hydrolysis of ethyl methyl-ethylacetoacetate according to the directions of Wislicenus (*Annalen*, 1883, 219, 303). It does not condense with cyanoacetamide, but gives with ethyl cyanoacetate a very small yield of the *ω*-imide of *αα'*-dicyano-*β*-methyl-*β*-ψ-butylglutaric acid (XXX, p. 692), a substance which crystallises from alcohol in magnificent, nacreous plates resembling naphthalene in appearance, and melting at 215—216°:

0.0827 gave 0.1860 CO<sub>2</sub> and 0.0471 H<sub>2</sub>O. C=61.33; H=6.33.

0.0553 „ 8.65 c.c. N<sub>2</sub> at 16.5° and 770 mm. N=18.36.

C<sub>13</sub>H<sub>15</sub>O<sub>2</sub>N<sub>3</sub> requires C=61.8; H=6.44; N=18.0 per cent.

#### *Benzylethylmethyl Ketone* (XXXI, p. 692).

The ketone required for this investigation was prepared according to Harries and Müller's method (*Ber.*, 1902, 35, 966). The yield of condensation product with ethyl cyanoacetate and

alcoholic ammonia was found to be exceedingly small—0.5 gram being obtained from 8.1 grams of the ketone. The *ω*-imide of *αα'*-dicyano-*β*-methyl-*β*-(*α*-benzylethyl)glutaric acid (XXXII, p. 692) crystallises from dilute alcohol in small needles melting at 223—224°:

0.1212 gave 0.3068 CO<sub>2</sub> and 0.0636 H<sub>2</sub>O. C=69.05; H=5.83.

C<sub>17</sub>H<sub>17</sub>O<sub>2</sub>N<sub>3</sub> requires C=69.2; H=5.8 per cent.

*Benzyl isopropyl Ketone* (XXXIII, p. 692).

The pure ketone was prepared by distilling together an intimate mixture of calcium phenylacetate and calcium isobutyrate in a current of carbon dioxide. The product was fractionated and separated into three main fractions, consisting of diisopropyl ketone, benzyl isopropyl ketone, and dibenzyl ketone. After refractionation, 30 grams of benzyl isopropyl ketone were obtained from 165 grams of calcium phenylacetate. The ketone boils at 238—240°. The *semicarbazone* is formed when a solution of semicarbazide acetate is mixed with the ketone, together with enough alcohol to bring the latter into solution, and the mixture allowed to remain overnight. It crystallises from alcohol in small, cubical crystals resembling common salt, and melts at 138° to a colourless, opaque liquid, which clears at 139°:

0.1454 gave 25.8 c.c. N<sub>2</sub> at 28° and 762.4 mm. N=19.38.

C<sub>12</sub>H<sub>17</sub>ON<sub>3</sub> requires N=19.2 per cent.

No condensation product could be obtained from this ketone either with cyanoacetamide or with ethyl cyanoacetate.

When a commercial preparation of the ketone was employed, a condensation product was obtained in poor yield; from this, two compounds were isolated by fractional crystallisation from alcohol. One of these crystallised in clusters of prismatic needles melting at 214—216°, and was proved by direct comparison to be identical with the benzylethyl compound (*q.v.*) (Found: C=68.21; H=5.36; N=15.17. C<sub>16</sub>H<sub>15</sub>O<sub>2</sub>N<sub>3</sub> requires C=68.3; H=5.3; N=14.9 per cent.).

The other compound can be obtained from the mother liquors after the above compound has separated out, although, with one sample of the ketone, it formed the greater part of the condensation product. It crystallised from alcohol in long, flattened needles melting at 246—247°, and was proved by direct comparison to be identical with the benzylmethyl compound (*q.v.*) (Found: C=67.53; H=5.09. C<sub>15</sub>H<sub>13</sub>O<sub>2</sub>N<sub>3</sub> requires C=67.4; H=4.9 per

cent.). This compound appears to be identical with the one described by Guareschi as the benzylisopropyl derivative (*Gazzetta*, 1918, 48, 97).

*Benzyl Ethyl Ketone* (XXXVII, p. 692).

A condensation product with ethyl cyanoacetate was readily obtained from this ketone, and was prepared for the sake of comparing it with that obtained from benzyl isopropyl ketone. We find the yield to be as high as 7.5 grams from 14.8 grams of the ketone (compare Guareschi, *Gazzetta*, 1918, 48, 92).

The  $\omega$ -imide of  $\alpha\alpha'$ -dicyano- $\beta$ -benzyl- $\beta$ -ethylglutaric acid (XXXVI, p. 692) crystallises from alcohol in fine, prismatic needles melting at 214—216° (Guareschi, *loc. cit.*, gives 222—226° as the melting point of this substance):

0.1192 gave 0.2984  $\text{CO}_2$  and 0.0566  $\text{H}_2\text{O}$ . C=68.27; H=5.28.

$\text{C}_{16}\text{H}_{15}\text{O}_2\text{N}_3$  requires C=68.3; H=5.3 per cent.

The products obtained by the acid hydrolysis of this imide appear to be abnormal, and are still under investigation.

*Benzyl Methyl Ketone* (XXXV, p. 692).

This ketone condenses very readily with ethyl cyanoacetate and gives a good yield (13 grams from 10 grams of the ketone) of the  $\omega$ -imide of  $\alpha\alpha'$ -dicyano- $\beta$ -benzyl- $\beta$ -methylglutaric acid (XXXIV, p. 692). It crystallises from alcohol in long, flattened needles, which melt at 246—247° and decompose a few degrees above this temperature:

0.1194 gave 0.2938  $\text{CO}_2$  and 0.0506  $\text{H}_2\text{O}$ . C=67.12; H=4.71.

0.1072 „ 0.2650  $\text{CO}_2$  (by  $\text{CrO}_3$  method). C=67.40.

$\text{C}_{15}\text{H}_{13}\text{O}_2\text{N}_3$  requires C=67.4; H=4.9 per cent.

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[Received, June 3rd, 1919.]



# LVIII.—"Blue John" and other Forms of Fluorite.

By BERTRAM BLOUNT and JAMES HARRY SEQUEIRA.

A GOOD deal of work has been done on the properties of fluorspar or fluorite in the various forms in which it occurs in nature. Fluorspar as an industrial substance is ably dealt with in a memoir of the Geological Survey, entitled "Special Reports on the Mineral Resources of Great Britain," by Messrs. Carruthers, Pocock, and May, to which Messrs. Dewey and Brownhead have contributed. In this pamphlet, no reference is made to the cause of the colour.

Derbyshire is properly regarded as the home of "Blue John." The famous Blue John mine is in the Castleton district, and is thus described. "The Blue John mine consists of a number of natural caverns in carboniferous limestone connected by tortuous pipes or fissures and extending for a great distance. The blue fluorspar or 'Blue John' occurs as a lining on the walls of fissures and pipes, or in concentrically arranged layers. It is associated with barytes, and a leader of this mineral is usually considered a good guide to a deposit of 'Blue John.' The so-called veins are irregular, flattened pipes running for a while almost horizontally, and then bending sharply up and down and cutting across the bedding. Where a vein is nearly flat, its upper and lower surfaces are lined by coatings of blue fluorspar. . . ." This is enough for the present purpose, and it may be accepted that this is the best account extant of the occurrence of "Blue John" in Great Britain.

There is not much that we have been able to discover in foreign literature except a paper by H. W. Morse (*Proc. Amer. Acad. Arts and Sci.*, 1906), which deals chiefly with the fluorescence of fluorite as studied in the spectroscope, but incidentally touches on some points of interest here. The essential statements are that the cause of the colour may be due to organic matter, and the conclusion arrived at is that "the question as to the cause of the colour of fluorspar still remains in this unsettled state." It is further said that the cause of the odour on heating is doubtful, and, further, that the gases expelled by this means are chiefly carbon dioxide, carbon monoxide, and hydrogen. Tests were made for helium on 10 kilos. of fluorite with a negative result, and the author of the paper feels so doubtful of his conclusion that towards the end of his paper he says: "I saw no reason to question the statement that the colour of fluorite is due to organic matter."

The evidence for and against this view is given in the ensuing notes of experiments made by ourselves.

*Chemical Composition of Blue John.*

Below are analysis of "Blue John" and of the white parts of the same mineral.

"Blue John."	Per cent.	White portions of same sample.
		Per cent.
Calcium fluoride .....	99.69	99.71
Alumina and ferric oxide .....	0.048	0.026
Manganese .....	nil	nil
Magnesia .....	0.006	0.005
Chlorine .....	nil	nil
Sulphur trioxide.....	nil	nil
Sulphur .....	trace	trace
Phosphorus .....	0.09	0.08

It will be seen that the difference between them is so small as to be almost inappreciable. It will also be noticed that metals such as manganese, which have been regarded as likely to be the cause of the colour, are practically absent.

The natural conclusion is that the colour of "Blue John" is due to some organic dye of animal origin, and that this has been absorbed by certain parts of the "Blue John" as distinct from others. Some support is given to this idea by the fact that there is usually a mechanical line of demarcation between the white and blue portions of typical pieces of "Blue John." This assumption of the cause of colour was tested by systematic extraction of "Blue John," powdered so as to pass a 60  $\times$  60 mesh sieve, with chloroform, toluene, and aniline. Chloroform extracted 0.11 per cent. of oily matter, toluene 0.04 per cent. of a similar substance, and aniline nothing further. Acetone, nitrobenzene, and naphthalene were also tried, with negative results; the extracted mineral remained as deep a blue as before extraction. A combustion of the extracted material gave C=0.046 per cent., showing that the amount of organic matter must be minute. The hydrogen was 0.17 per cent., but this is probably due to a small quantity of water combined or occluded, and the same remark may apply to the carbon, which may have existed as liquid carbon dioxide in the crystals. The "Blue John" after combustion was colourless.

It may be remarked that all these experiments were made on the mineral direct from the mine. Earlier experiments were made on "Blue John" prepared as ornaments, and at that time the authors were not aware that the handsomest specimens are filled with resinous matter in order to make them easier to handle and

to turn. Probably on this account other chemists have been misled into the belief that the colouring material is organic, because they have found organic matter in the samples which they examined, and supposed that it was of natural origin. It remains a fact, however, that organic matter exists in "Blue John." This organic matter is not affected by a temperature of  $150^{\circ}$ . When a temperature of about  $350^{\circ}$  is reached, the "Blue John" decrepitates and the colour disappears.

#### *Gases from "Blue John."*

On account of experiments, which will be described later, it was supposed that the colour of "Blue John" might be due to the action of radium, and many trials were made in this direction. As is well known, glass is easily coloured by the rays from radium, and a series of experiments was made by one of us.

While these experiments were proceeding, another method was adopted for the same end. A fairly large quantity (about 50 grams) of "Blue John" direct from the mine, not impregnated by any extraneous resinous material, was heated in a hard glass tube, and the gases were pumped out. After the carbon dioxide, hydrogen, and nitrogen had been removed, the remaining inert gases were examined spectroscopically in a Plücker tube. Argon was present, but helium was not. The deduction is that the gases consisted only of those that occur naturally in rocks and minerals which readily decrepitate.

#### *Green Fluorspar "Green John."*

This is similar to "Blue John," but decrepitates with greater violence. Both varieties fluoresce on heating, the light from the green kind being more vivid. Green fluorspar, called conveniently "Green John," and so referred to hereafter, appears to be much rarer than "Blue John," and it was only by the kindness of a friend that a specimen of good quality was obtained. Others taken from mines in Durham and Cornwall were evidently less pure. As the quantity of good "Green John" available was somewhat small, our examination of it was necessarily limited, and the gases which are given off on decrepitation were not analysed, the quantity at our disposal being too small for any satisfactory examination.

Systematic experiments by one of us (J. H. S.) were carried out at the London Hospital on the action of radium and X-rays

on various samples of fluorspar. The notes made at the time are here recorded.

(A) *"Blue John": Experiments with Radium.*

(1) Two pieces of banded fluorspar ("Blue John") were exposed to radium, contact being made with a plate 2.5 cm. square containing 30 milligrams of radium salt under a varnish.

As a result of this exposure, both pieces of spar changed colour, the white parts becoming bright blue and the blue becoming darker. In ten days these changes were well marked.

(2) Pieces of "Blue John," "Green John," and white fluorspar were similarly exposed. In three days, a bright blue change was noticed in the white fluorspar, the "Green John" was slightly darker, and the "Blue John" much darker.

(3) Portions of "Blue John" were heated in glass tubes, and thereby decolorised. These decolorised specimens were then exposed to radium and to X-rays. The specimen exposed to radium for fourteen days became a light blue. The specimen exposed to X-rays for about twenty-four hours continuously became dark purple.

(4) A small portion of "Blue John," banded, was exposed for six hours to X-rays, and turned almost a dark violet colour.

The "Green John" exposed for fourteen days was distinctly darker in colour.

(B) *Experiments with X-Rays.*

(1) Half an hour's exposure at 7.5 cm. produced on:

"Blue John," slight deepening.

"Green John," no change.

Fluorspar, change to violet shade.

The fluorspar, on being replaced in a drawer, returned to almost normal colour.

(2) Half an hour's exposure at 7.5 cm. produced on:

"Blue John," slight deepening.

"Green John," no change.

Fluorspar, change to violet shade.

The fluorspar returned to almost normal colour.

(3) Forty-five minutes' exposure at 7.5 cm. produced on:

"Blue John," more marked change.

"Green John," no change.

Fluorspar, more marked change.

The fluorspar almost recovered.

- (4) Ten minutes' exposure at 7.5 cm. produced on:  
Fluorspar, light violet colour.  
No other change perceptible.
- (5) Half an hour's exposure at 7.5 cm. produced on:  
"Green John," fluorescence.  
Fluorspar, change as before.

The "Green John," after being carried into a dark room, still fluoresced for about three or four minutes.

Fluorspar in a glass tube also fluoresced, but very slightly.

- (6) Ten minutes' exposure at 7.5 cm. produced on:  
"Green John," slight fluorescence (both).

Material after resting for fourteen days:

Fluorspar was pink with one mauve spot.

"Blue John" was darker than when experiments started.

"Green John" did not appear to have changed at all.

The fluorspar in glass was darker than at first.

None of the specimens exposed to X-rays made any change in photographic plates, even after prolonged exposure.

Even after colour changes had been produced by exposures to X-rays and radium, there was no evidence of radioactivity, as shown by exposure of a photographic plate.

From these experiments, it appears that there is no substantial difference between white fluorspar and "Blue John," except in respect of the small amount of organic matter which gives the colour of "Blue John."

The same seems to hold for "Green John" and for the amethystine varieties. It appears that the colouring matter is, after all, organic. The influence of X-rays and of radium on natural fluorspar appears similar to that on glass. The *causa causans* is unknown.

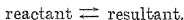
From a series of experiments which have now lasted more than two years, there is no reason to suppose that what in the earlier trials seemed to be a reasonable hypothesis, namely, that the colour of "Blue John" and other varieties of coloured fluorspar owes its origin to radioactive effect, has no foundation.

LIX.—*Studies in Catalysis. Part XI. The Le Chatelier-Braun Principle from the Point of View of the Radiation Hypothesis.*

By WILLIAM CUDMORE McCULLAGH LEWIS.

THE object of this note is to point out that the quantum-radiation view of chemical reactivity is in agreement with the thermodynamic principle of Le Chatelier and Braun as applied to the effect of temperature on the equilibrium constant of a reversible reaction.

Consider the reversible reaction:



Let us suppose that the reaction from left to right is endothermic. Then, in accordance with the principle of mobile equilibrium, an increase in temperature will favour the resultants.

From the point of view of radiation, the fact that the above process is endothermic means that the critical increment of the resultant is less than that of the reactant. This follows from the quantum-heat expression:

heat evolved = critical increment of resultant *minus*  
critical increment of reactant,

or heat evolved =  $Nh(\nu_2 - \nu_1)$ , where  $N$  is the Avogadro number and  $h$  is Planck's constant. In the case considered, it follows that the critical frequency  $\nu_2$  of the resultant is less than the critical frequency  $\nu_1$  of the reactant.

Let us consider the above equilibrium at two different temperatures,  $T_1$  and  $T_2$ , where  $T_1$  is less than  $T_2$ . For the short infra-red region (which has already been shown to be of significance for reactions which proceed with measurable velocity at the ordinary temperature), as well as for the visible and ultra-violet regions, the radiation density corresponding with the frequency  $\nu_1$  at  $T_1$  is

$$\frac{8\pi h \nu_1^3 n^3}{c^3} e^{-h\nu_1/kT_1},$$

and at  $T_2$  the density is

$$\frac{8\pi h \nu_1^3 n^3}{c^3} e^{-h\nu_1/kT_2},$$

where  $c$  is the velocity of light in a vacuum.

If  $T_1$  and  $T_2$  are not very far apart, and especially if the react-

ing system is gaseous, the refractive index term  $n$  will be practically the same at both temperatures.

The fractional increase in the radiation density, due to the rise in the temperature from  $T_1$  to  $T_2$  at the frequency  $\nu_1$ , is given by

$$\frac{\frac{8\pi h \nu_1^3 n^3}{c^3} (e^{-h\nu_1/kT_2} - e^{-h\nu_1/kT_1})}{\frac{8\pi h \nu_1^3 n^3}{c^3} e^{-h\nu_1/kT_1}},$$

which is equal to

$$\left( e^{\frac{h\nu_1}{k} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)} - 1 \right).$$

Similarly, for the fractional increase in the radiation density at the frequency  $\nu_2$  we obtain

$$\left( e^{\frac{h\nu_2}{k} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)} - 1 \right).$$

Since by hypothesis  $\nu_1$  is greater than  $\nu_2$ , it follows from the above expressions that the fractional increase in the radiation density at the frequency  $\nu_1$  is greater than that at the frequency  $\nu_2$ . Hence at the higher temperature the radiation density of the type absorbable by the reactant ( $\nu_1$ ) has increased *relatively* to that absorbable by the resultant ( $\nu_2$ ).

On the radiation hypothesis of chemical reactivity, it is assumed that the rate of decomposition is directly proportional to the radiation density. For both frequencies, the rise in temperature has caused an increase in the radiation density, but the increase is relatively greater for the higher frequency ( $\nu_1$ ) as compared with the lower frequency ( $\nu_2$ ). It follows, therefore, that at the higher temperature both the reactant and the resultant react or decompose more rapidly than they do at the lower temperature. This is in agreement with experiment. What is more important, however, is that the reactant decomposes at a relatively faster rate than the resultant, because the radiation density of the reactant is relatively increased with respect to that of the resultant. Hence as the temperature is raised, the existence of the resultant, in the above case, is favoured more than that of the reactant, and the equilibrium position shifts over towards the right. Had the reaction been exothermic, the relative positions of  $\nu_1$  and  $\nu_2$  would have been reversed, with the result that the equilibrium concentration of the reactant would have increased relatively to that of the resultant.

These conclusions are identical with those which are arrived at

on the basis of the principle of Le Chatelier and Braun. The radiation hypothesis is therefore in complete agreement with the thermodynamic generalisation; and, in fact, the conclusion regarding the direction of the change in the equilibrium position with temperature could be inferred on the radiation basis alone, without any direct appeal to thermodynamics.

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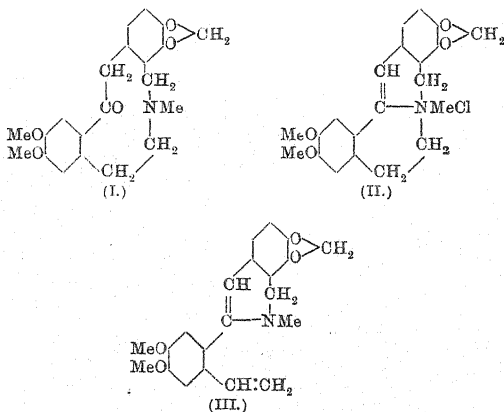
[Received, May 29th, 1919.]



LX.—*Cryptopine. Part II.*

By WILLIAM HENRY PERKIN, jun.

THE present investigation was originally undertaken with the object of clearing up some points, difficult of explanation, which had arisen during the course of the experiments described in Part I of this research.\* Gradually the scope of the inquiry has widened, and many developments are included in this communication which were at first not contemplated. Broadly speaking, the basis of the new material is the series of changes represented by the conversion of cryptopine (I) into *isocryptopine* chloride (II), and the formation of anhydrocryptopine (III) from the latter by the elimination of hydrogen chloride (833, 850).†

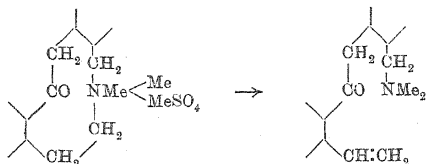


It was shown in the earlier research (852) that the properties of anhydrocryptopine are in many respects quite unusual, and one of the points most difficult of explanation is the behaviour of anhydrocryptopine methosulphate (or the corresponding methochloride) towards hydrolytic agents. Normally, the hydrolytic

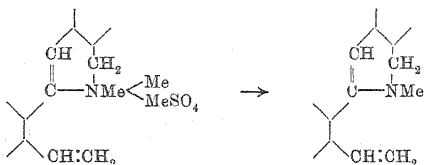
\* "Cryptopine and Protopine," Part I., T., 1916, 109, 815—1028.

† The numbers in brackets—thus (833)—refer to the page in Part I.

decomposition of a methosulphate results in the formation of a new base containing a methyl group more than the original base contained. Thus cryptopine methosulphate is decomposed on hydrolysis with the formation of methylcryptopine (847).



The methosulphate of anhydrocryptopine does not behave in this way (852), but is hydrolysed by methyl-alcoholic potassium hydroxide with elimination of the added methyl group and regeneration of anhydrocryptopine.

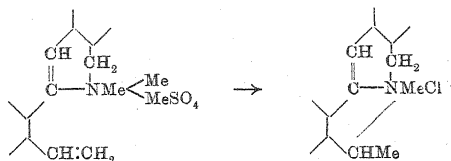


A case of this kind does not appear to have been previously recorded, and although an attempt was made (854; T., 1918, 113, 735) to find some explanation for this curious removal of a methyl group from nitrogen, it is still not clear why the *N*-methyl-dihydro-isoquinoline ring characteristic of anhydrocryptopine should exhibit this unusual behaviour. Recently (T., 1918, 113, 735), a welcome confirmation of the curious change just mentioned has been forthcoming, since it has been found possible to prepare from berberine the derivative—anhydromethylberberine—which corresponds exactly with anhydrocryptopine.

This substance also combines readily with methyl sulphate to yield the corresponding methosulphate, which, when boiled with methyl-alcoholic potassium hydroxide, is decomposed in exactly the same manner as anhydrocryptopine methosulphate, with regeneration of anhydromethylberberine.

Not only do alkali hydroxides cause the elimination of a *N*-methyl group from anhydrocryptopine methosulphate, but experiment has shown that a process of the same kind occurs even

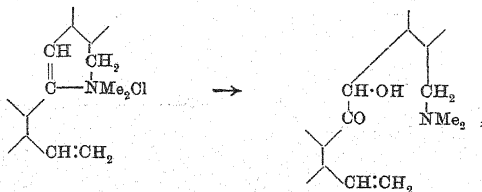
more readily when acid reagents are employed. Thus anhydrocryptopine methosulphate is rapidly changed by boiling with concentrated hydrochloric acid, and  $\psi$ -cryptopine chloride is produced, a decomposition which appears to be correctly represented by the scheme (855):



An exactly analogous change is observed when anhydromethylberberine methosulphate is digested with concentrated hydrochloric acid,  $\psi$ -methylberberinium chloride being obtained (T., 1919, 113, 735).

In the present communication (p. 767), it is shown that concentrated mineral acid need not be employed in order to bring about the elimination of the *N*-methyl group, since  $\psi$ -cryptopine chloride is readily obtained when anhydrocryptopine methosulphate is heated on the steam-bath with dilute hydrochloric acid, and  $\psi$ -cryptopine hydrogen sulphate,  $C_{21}H_{22}O_4N \cdot HSO_4$ , results, in a similar manner, from the action of dilute sulphuric acid on the methosulphate.

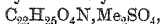
The remarkable changes associated with the action of hydrolytic agents on anhydrocryptopine methosulphate suggested the desirability of making a further study of the behaviour of this substance towards other reagents. Experiments on the oxidation of the methosulphate did not lead to useful results, but the corresponding methochloride is oxidised by permanganate, without elimination of an *N*-methyl group and with the formation of a base,  $C_{22}H_{25}O_6N$  (m. p.  $188^\circ$ ), which appears to be produced according to the scheme:



and has been named *dioxymethylisoanhydrodihydrocryptopine* (p. 738).

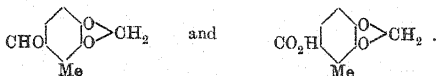
Of much greater interest is the behaviour of anhydrocryptopine methosulphate when subjected to the action of reducing agents, and it was the results obtained during the study of these remarkable changes which led to the extension of the subject so as to include the action of reducing agents on other derivatives of cryptopine. In order that this complex study may be made as clear and concise as possible, the subject has been divided into sections, and the sectional numbers in this summary correspond with the numbers of the sections in the experimental part.

*Section I (a). The Reduction of Anhydrocryptopine Methosulphate by Sodium Amalgam in Alkaline Solution* (p. 740).—When sodium amalgam is added to the aqueous solution of anhydrocryptopine methosulphate, a base,  $C_{22}H_{25}O_4N$ —*dihydroanhydromethylcryptopine*—gradually separates, which has not been obtained crystalline, but yields a crystalline methosulphate,

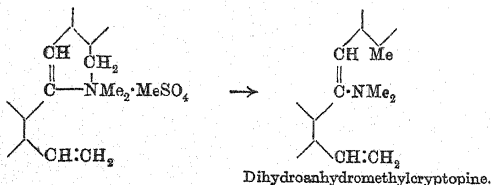


and methiodide,  $C_{22}H_{25}O_4N, MeI$ . It is clear, therefore, that elimination of a methyl group had not taken place during reduction under these conditions.

On oxidation in acetone solution with permanganate, the new base yields 5:6-methylenedioxy-*o*-tolualdehyde (907) and 5:6-methylenedioxy-*o*-toluic acid (916),

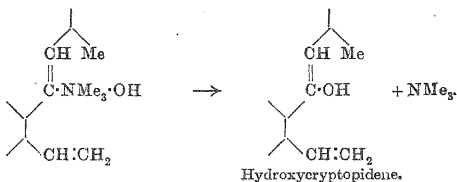


It is clear, therefore, that its formation from anhydrocryptopine methosulphate is probably represented thus:

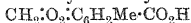


a view which has received support from the detailed investigation of the base. It has already been stated that the base yields a crystalline methosulphate, and this is readily decomposed by boil-

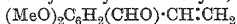
ing with methyl-alcoholic potassium hydroxide, with elimination of trimethylamine and formation of a new substance,  $C_{20}H_{20}O_5$ :



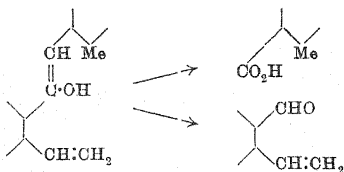
*Hydroxycryptopidene*\* melts at 88—90°, and yields, on oxidation with permanganate, 5:6-methylenedioxy-*o*-toluic acid,



(916), and 4:5-dimethoxy-2-vinylbenzaldehyde,

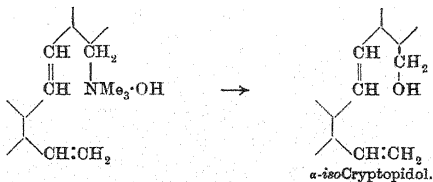


(904), the former containing the upper and the latter the lower portion of the molecule.



This fission clearly demonstrates the constitution of the substance,  $C_{20}H_{20}O_5$ , and indirectly that also of dihydroanhydromethyl-cryptopine.

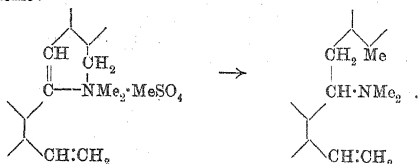
Hydroxycryptopidene is isomeric and closely allied with  $\alpha$ -isocryptopidol (m. p. 92°; 843), which results in a similar manner from methylisocryptopidol methosulphate by the elimination of trimethylamine:



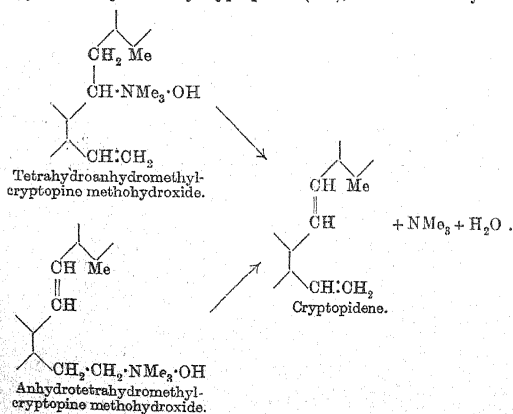
\* Compare (926) for a description of the parent substance cryptopidene.

Hydroxycryptopidene does not yield an acetyl derivative, but is converted by the action of acetyl chloride into a polymeric modification,  $(C_{20}H_{20}O_5)_n$ , which melts at about  $200^\circ$ , and corresponds closely in properties and composition with the  $\beta$ -modification of isocryptopidol (843).

*Section I(b). The Reduction of Anhydrocryptopine Methosulphate by Sodium Amalgam in Acid Solution* (p. 743).—When anhydrocryptopine methosulphate is reduced by sodium amalgam in the presence of a large excess of hydrochloric acid, disruption of the central ring takes place in a manner similar to that described in Section I(a), but with the addition of four atoms of hydrogen and again without the elimination of a methyl group. The product is a base,  $C_{20}H_{27}O_4N$ —*tetrahydroanhydromethylcryptopine*—and its properties are in harmony with its formation, according to the scheme:

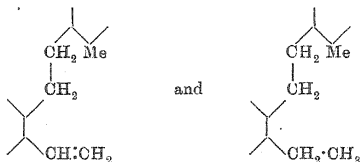


This base has not been obtained crystalline, and is isomeric with anhydrotetrahydromethylcryptopine (898), which is crystalline



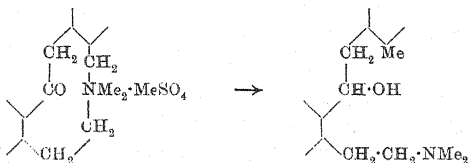
and melts at  $107^{\circ}$ . The close relationship between these bases is well brought out when their formulæ are written side by side and by the fact that the methosulphates of both are decomposed by boiling with methyl-alcoholic potassium hydroxide, with elimination of trimethylamine and separation of cryptopidene (m. p.  $123^{\circ}$ ; see above).

A further stage in the reduction of the cryptopine molecule has been achieved by the preparation of *dihydrocryptopidene*,  $C_{20}H_{22}O_4$  (m. p.  $128^{\circ}$ ), and the reduction of cryptopidene to *tetrahydrocryptopidene*,  $C_{20}H_{24}O_4$ :



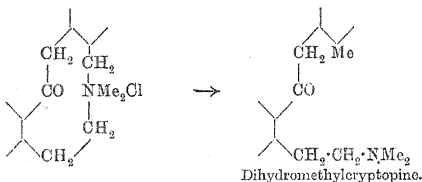
The first of these is obtained by a process described on p. 762, and the latter is produced when cryptopidene is reduced in boiling alcoholic solution with sodium. It is one of the most beautiful substances in the cryptopine series, melts at  $78^{\circ}$ , and crystallises in stout, colourless prisms (p. 745).

*Section II (p. 746). The Reduction of Cryptopine Methochloride in Alkaline Solution.*—The conversion of cryptopine methosulphate into tetrahydromethylcryptopine by reduction in strongly acid



solution with sodium amalgam is described in Part I of this research (821 and 826), and the present object was to determine whether, during this process, the reduction of the keto-group precedes the fission of the ring or vice versa. Since further experiments on the reduction of the methosulphate did not yield information of value, the effect of reducing agents on the corresponding methochloride was investigated. The interesting fact was then observed that, whilst cryptopine methochloride, when reduced in alkaline solution with sodium amalgam, is converted in the

main into tetrahydromethylcryptopine, there is also formed in small quantity a new base,  $C_{22}H_{27}O_5N$ , which melts at  $118-120^\circ$ , and is obviously produced according to the scheme:



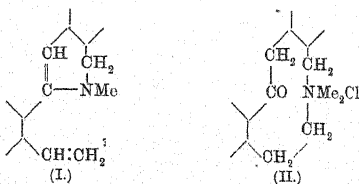
that is to say, during its formation, the ten-membered ring has been ruptured before the reduction of the keto-group.

The constitution assigned to dihydromethylcryptopine receives support from the fact that, when oxidised with permanganate, the base yields 5:6-methylenedioxy-*o*-tolualdehyde and 5:6-methylenedioxy-*o*-toluic acid (compare p. 747). The isolation of this base would seem to indicate that the first action of the alkaline reducing agent on cryptopine methochloride is fission of the ten-membered ring, but that most of the dihydromethylcryptopine, thus produced, suffers further reduction before it can be removed from the sphere of action of the excess of the reducing agent.

### Section III.

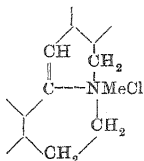
#### *The Reduction of isoCryptopine Chloride.*

In the cases discussed in Sections I and II, the groups of atoms taking part and suffering disruption as the result of reduction belong in I to a single dihydroisoquinoline nucleus, and in II to the ten-membered group characteristic of cryptopine:



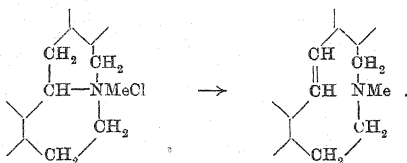
It was next desired to investigate what the effect of reduction might be in the case of a substance containing a partly reduced double isoquinoline ring, and *isocryptopine* chloride (833) was



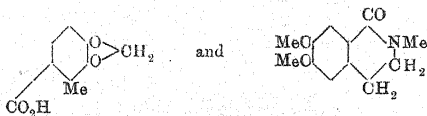


selected for this purpose. The effect of reduction was again studied (a) in alkaline and (b) in acid solution.

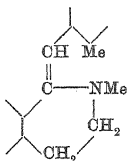
*Section III (a). The Reduction of isocryptopine Chloride in Alkaline Solution* (p. 748).—Since isocryptopine chloride is very sparingly soluble in cold water, the reduction with sodium amalgam could only be carried out effectively on the steam-bath, and, under these conditions, a resinous base separates, and the liquid, on cooling, becomes filled with a voluminous mass of needles of a quaternary salt. This salt, which is produced in considerable quantity, was readily identified as isodihydrocryptopine  $\beta$ -chloride, since, on boiling with methyl-alcoholic potassium hydroxide, it yielded anhydridihydrocryptopine (4) (938):



One of the main directions in which isocryptopine chloride suffers reduction is therefore simply by the addition of hydrogen to the double linking without disruption of either ring. The resinous base may be separated, by fractional crystallisation, into two new substances, namely, a very sparingly soluble base,  $C_{21}H_{25}O_4N$ , melting at  $195^\circ$ , which is present in very small quantity, and considerable quantities of a readily soluble base,  $C_{21}H_{25}O_4N$ , which melts at  $138^\circ$ . The base,  $C_{21}H_{25}O_4N$ , yields, on oxidation, 5:6-methylenedioxy-*o*-toluic acid (916), and apparently



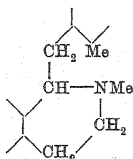
also 1-keto-6:7-dimethoxy-2-methyltetrahydroisoquinoline (Pyman, T., 1909, 95, 1268), and must therefore have the constitution



Dihydroanhydroisocryptopine.

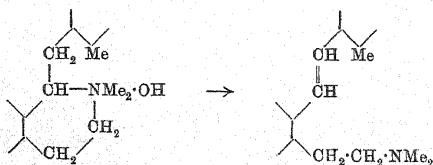
This base is therefore produced from *isocryptopine* chloride by the rupture of the upper dihydroisoquinoline ring without reduction of the double linking.

The readily soluble base,  $C_{21}H_{25}O_4N$ , melting at  $138^\circ$ , yields 5:6-methylenedioxy-*o*-tolualdehyde (and acid), as well as 1-keto-6:7-dimethoxy-2-methyltetrahydroisoquinoline, on oxidation with permanganate, and must therefore be the dihydro-derivative of the base just described (m. p.  $195^\circ$ ) and have the constitution



Tetrahydroanhydroisocryptopine.

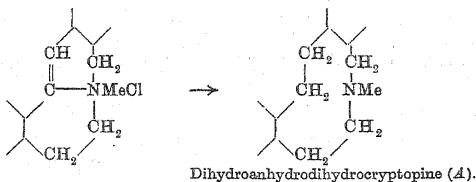
It yields very characteristic salts and other derivatives, of which the *methosulphate*,  $C_{21}H_{25}O_4N, Me_2SO_4$  (m. p.  $160^\circ$ ), and *methiodide*,  $C_{21}H_{25}O_4N, MeI$  (m. p.  $263^\circ$ ), crystallise particularly well. When boiled with methyl-alcoholic potassium hydroxide, the methosulphate is readily decomposed, with the formation of anhydrotetrahydromethylcryptopine, a base which had previously



been obtained, in the form of its hydrochloride, from tetrahydro-methyleryptopine by the action of phosphoryl chloride (899).

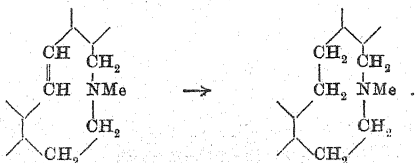
*Section III (b). The Reduction of isoCryptopine Chloride in Acid Solution* (p. 749).—Reduction takes place readily when the hot solution of *isocryptopine* chloride in a mixture of dilute acetic and hydrochloric acids is treated with a large excess of sodium amalgam, and leads to the formation of two bases,  $C_{21}H_{25}O_4N$ , melting at  $138^\circ$  and  $164^\circ$  respectively, as well as of considerable quantities of *isodihydrocryptopine*  $\beta$ -chloride.

The base melting at  $138^\circ$  is tetrahydroanhydro*isocryptopine*, identical with that isolated from the product of the alkaline reduction of *isocryptopine* chloride. The second base, melting at  $164^\circ$ , which does not appear to be one of the products of the alkaline reduction, is *dihydroanhydrodihydrocryptopine* (A), and, in its formation, not only has the ethenoid linking in *isocryptopine* been reduced, but the double *isoquinoline* ring has also suffered disruption in a very remarkable manner, with the formation of a fully saturated ten-ring system.

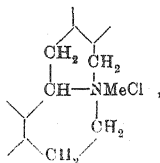


This base is remarkably stable to permanganate, and does not yield 5:6-methylenedioxy-*o*-toluic acid on oxidation, showing that reduction has not resulted in the formation of the group  $CH_2:O_2:C_6H_2Me:CH:$  (p. 716).

The definite proof of its constitution was obtained as the result of the observation that the base in question is readily produced when anhydrodihydrocryptopine (A) (938) is reduced by sodium amalgam in acid solution.

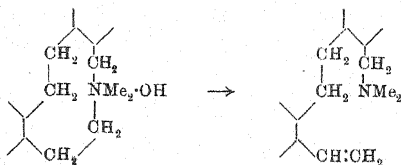


The curious formation of dihydroanhydrodihydrocryptopine (A) from *isocryptopine* chloride by reduction is dependent in some way on the presence of the ethenoid linking in one of the reduced *isoquinoline* rings, a condition which apparently causes strain, and consequent instability. That this is so is indicated by the fact that, when this ethenoid linking is not present, scission does not appear to take place. Thus, for example, all attempts to reduce tetrahydroberberine methochloride, which contains the grouping

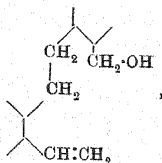


have been unsuccessful.

Dihydroanhydrodihydrocryptopine (A) yields a methosulphate,  $\text{C}_{21}\text{H}_{25}\text{O}_4\text{N}, \text{Me}_2\text{SO}_4$ , which, on hydrolysis with methyl-alcoholic potassium hydroxide, is converted into *dihydroisoanhydrodihydro-methylcryptopine*,  $\text{C}_{22}\text{H}_{27}\text{O}_4\text{N}$  (945), a beautiful substance melting at  $77^\circ$ , the crystals of which have been measured (p. 757).

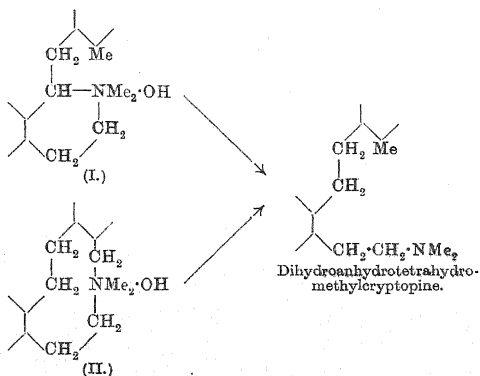


Finally, the methosulphate of this base,  $\text{C}_{22}\text{H}_{27}\text{O}_4\text{N}, \text{Me}_2\text{SO}_4$ , is decomposed by boiling with methyl-alcoholic potassium hydroxide, with the separation of *dihydro- $\alpha$ -isocryptopidol*,

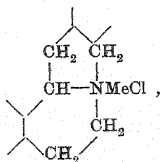


a rather indefinitely crystalline substance which is clearly the dihydro-derivative of  *$\alpha$ -isocryptopidol* (948).

*Section III (c). Dihydroanhydrotetrahydromethylcryptopine* (p. 759).—This substance is produced from the methosulphate either of tetrahydroanhydroisocryptopine (I, m. p. 138°, p. 722) or of dihydroanhydrodihydrocryptopine (A) (II, m. p. 164°, p. 723) by reduction in alkaline solution with sodium amalgam:



The other cases of ring-fission during reduction, described in this communication, occur in systems in which the ring in question is unsaturated, and it is pointed out on p. 724 that attempts to reduce the completely saturated system,

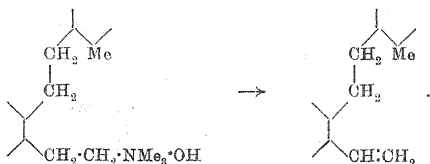


contained in tetrahydroberberine methochloride, have not been successful.

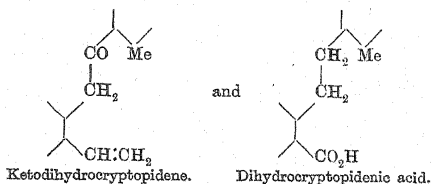
It is therefore remarkable that the removal of a bridge in this complex in the two directions shown in formulae I and II should so weaken the structure as to make it susceptible to reduction. It is, of course, possible that the accumulation of methyl groups on the nitrogen atom may tend to weaken the structure, and a good

deal of evidence is to be found in this communication in favour of that view.

*Dihydroanhydrotetrahydromethylcryptopine* melts at  $63^{\circ}$ , and is characterised by yielding a very sparingly soluble hydrochloride. The *methosulphate*,  $C_{23}H_{29}O_4N, Me_3SO_4$ , is decomposed by boiling with methyl-alcoholic potassium hydroxide, with elimination of trimethylamine and formation of *dihydrocryptopidene*.



This new derivative of cryptopidene (926) crystallises splendidly, melts at  $126-128^{\circ}$ , and yields the following interesting substances on oxidation with permanganate:



*Ketodihydrocryptopidene* melts at  $116^{\circ}$  and yields a *semicarbazone*,  $C_{21}H_{25}O_5N_3$ , melting at  $190^{\circ}$ . *Dihydrocryptopidenic acid* is a very sparingly soluble, crystalline acid (m. p.  $194-195^{\circ}$ ), the *anilide* of which,  $C_{18}H_{19}O_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$ , crystallises in needles and melts at  $185^{\circ}$ .

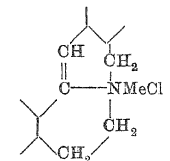
The degradation of cryptopine to this acid is particularly interesting, and it is unfortunate that the small amount of material available did not allow of its detailed investigation.

#### Section IV.

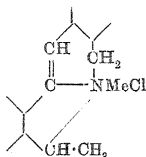
##### *The Reduction of $\psi$ -Cryptopine Chloride.*

The conversion of anhydrocryptopine methosulphate into  $\psi$ -cryptopine chloride is mentioned on p. 715 (compare 855 and 984), and the similarity in constitution between this substance and

*isocryptopine* chloride is obvious when their formulæ are compared:



*iso*Cryptopine chloride.



$\psi$ -Cryptopine chloride.

The essential difference between these formulæ is the fact that, whereas in *isocryptopine* chloride the central portion consists of two reduced *isoquinoline* rings fused together, the molecule of  $\psi$ -cryptopine chloride contains only one such ring. When the bridge across the molecule is removed by reduction, the result in the case of *isocryptopine* chloride is the formation of a ten-membered ring (p. 723), whereas if a similar change is assumed to take place in the molecule of  $\psi$ -cryptopine chloride, reduction should lead to the formation of a nine-membered ring system, of which, so far, few examples have been described.

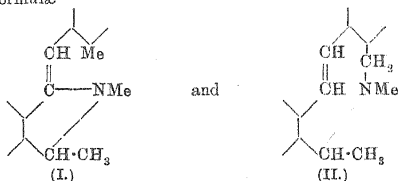
Since the investigation of this matter seemed to offer attractive possibilities, the problem has been carefully studied, and it may be said at once that the comparatively slight difference in constitution which  $\psi$ -cryptopine chloride exhibits in comparison with *isocryptopine* chloride is sufficient to give rise to wide differences in behaviour when the two substances are reduced under similar conditions.

*Section IV (a). The Reduction of  $\psi$ -Cryptopine Chloride in Alkaline Solution* (p. 769).— $\psi$ -Cryptopine chloride,  $C_{21}H_{23}O_4NCl$ , is readily reduced in slightly alkaline aqueous solution by sodium amalgam at the temperature of the steam-bath, and a base,  $C_{21}H_{23}O_4N$ , separates, which crystallises from methyl alcohol in stout prisms and melts at  $112^\circ$ .\*

This base is produced by the addition of two atoms of hydrogen to  $\psi$ -cryptopine chloride and elimination of hydrogen chloride, a

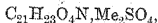
\* In the reduction of *isocryptopine* chloride, much *isodihydrocryptopine*  $\beta$ -chloride is always obtained by the direct reduction of the ethenoid linking (p. 721), but the corresponding *isodihydro*- $\psi$ -cryptopine chloride does not appear to be one of the products of the reduction of  $\psi$ -cryptopine chloride. Still more striking is the observation that, whereas during the reduction of *isocryptopine* chloride, the base formed in much the larger quantity is tetrahydroanhydro*isocryptopine*,  $C_{21}H_{25}O_4N$ , in the case of  $\psi$ -cryptopine chloride the reduction does not appear to proceed beyond the formation of the base  $C_{21}H_{23}O_4N$  (m. p.  $112^\circ$ ).

process which might take place in two different directions, leading to the formulæ



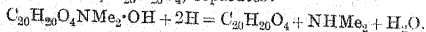
Judging from the course the reduction takes in the analogous case of *isocryptopine* chloride, the new base should correspond in constitution with dihydroanhydro*isocryptopine* (m. p. 195°, p. 722), that is to say, it should have the constitution represented by the partial formula I.

The investigation of the base has, however, shown that this is not the case. It does not, for example, yield 5:6-methylenedioxy-*o*-toluic acid,  $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_2\text{Me}\cdot\text{CO}_2\text{H}$  (p. 721), on oxidation with permanganate, and it can therefore scarcely contain the grouping,  $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_2\text{Me}\cdot\text{CH}$ , which is present in I. The alternative is that its constitution is that represented by formula II, and for this reason the base,  $\text{C}_{21}\text{H}_{23}\text{O}_4\text{N}$ , melting at 112°, has been named *ψ-anhydrodihydrocryptopine* (A) to indicate its relationship to anhydrodihydrocryptopine (A) (841). This base combines readily with methyl sulphate, and both the methosulphate,

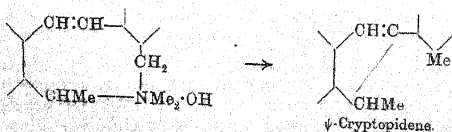


and the corresponding methiodide,  $\text{C}_{21}\text{H}_{23}\text{O}_4\text{N}\cdot\text{MeI}$ , are beautifully crystalline substances characterised by yielding highly coloured products on decomposition with methyl-alcoholic potassium hydroxide, which are obviously of complex nature and have not been further investigated.

When, however, the alkaline solution of the methosulphate is reduced by sodium amalgam, a remarkable change takes place, and a neutral substance,  $\text{C}_{20}\text{H}_{20}\text{O}_4$ , separates:



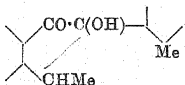
It is probable that this curious decomposition takes place in the following direction:



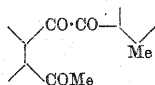


and, since the new substance, which crystallises beautifully and melts at  $144^{\circ}$ , is isomeric with cryptopidene (926; compare p. 772), it has been named  *$\psi$ -cryptopidene*.

An attempt was made to establish the constitution of the substance by studying its behaviour on oxidation with permanganate, but with partial success only. One of the substances produced is 5:6-methylenedioxy-*o*-toluic acid, the formation of which is in harmony with the suggested constitution. The principal products of oxidation are, however, *dioxy- $\psi$ -cryptopidene*,  $C_{20}H_{18}O_6$  (m. p.  $138-140^{\circ}$ ), and *trioxy- $\psi$ -cryptopidene*,  $C_{20}H_{18}O_7$  (m. p.  $165^{\circ}$ ). Both these substances exhibit a reaction reminiscent of the benzil reaction, that is to say, on boiling with methyl-alcoholic potassium hydroxide they dissolve to brown solutions which, in contact with air, become pink and gradually fade; the addition of hydrochloric acid then causes the precipitation of crystalline acids. Dioxy- $\psi$ -cryptopidene yields a *semicarbazone*,  $C_{21}H_{21}O_6N_3$ , and trioxy-cryptopidene a *disemicarbazone*,  $C_{22}H_{24}O_7N_6$ , so that if the formula assigned to  $\psi$ -cryptopidene is correct, it is probable that these oxidation products may have the partial formulæ

Dioxy- $\psi$ -cryptopidene.

and

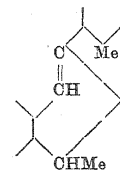
Trioxy- $\psi$ -cryptopidene.

*Section IV (b). The Reduction of  $\psi$ -Cryptopine Chloride in Acid Solution* (p. 774).—It has just been explained that the methosulphate of  $\psi$ -anhydrodihydrocryptopine (A) undergoes a curious decomposition when it is reduced in alkaline solution, with loss of the nitrogen atom as dimethylamine and formation of a neutral substance,  $C_{20}H_{20}O_4$  ( $\psi$ -cryptopidene).

It is perhaps still more remarkable that  $\psi$ -cryptopine chloride itself should, on reduction in acid solution with sodium amalgam, undergo a partial change in a similar direction, with elimination of the nitrogen atom, evidently as methylamine, and separation of a beautifully crystalline substance,  $C_{20}H_{20}O_4$ , which is isomeric with  $\psi$ -cryptopidene (m. p.  $144^{\circ}$ ), melts at  $152^{\circ}$ , and has been named *iso- $\psi$ -cryptopidene*. Since the melting points of the two substances do not greatly differ, it was at first thought that *iso- $\psi$ -cryptopidene* might possibly be  $\psi$ -cryptopidene in a very pure condition; but this is not the case, because the mixture of the two substances melts at about  $130^{\circ}$ . On oxidation with permanganate, *iso- $\psi$ -cryptopidene* yields considerable quantities of 5:6-methylenedioxy-*o*-tolualdehyde (m. p.  $72-74^{\circ}$ ), as well as of the corresponding acid (m. p.  $216^{\circ}$ ; compare p. 777), and also a substance,

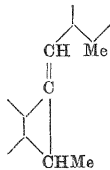
$C_{20}H_{20}O_5$  (*ketodihydroiso-ψ-cryptopidene*), which melts at  $135^\circ$  and yields a *semicarbazone*,  $C_{21}H_{23}O_5N_3$ .

The isomerism of *ψ-cryptopidene* and *iso-ψ-cryptopidene* is difficult to understand, but, as both yield 5:6-methylenedioxy-*o*-toluic acid on oxidation, it is suggested that the relationship may be that indicated by the formulæ



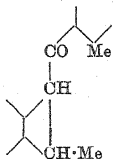
*ψ*-Cryptopidene.

and

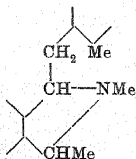


*iso-ψ*-Cryptopidene.

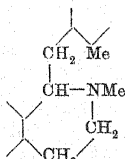
and it is probable that *ketodihydroiso-ψ-cryptopidene* contains the grouping:



The main product of the reduction of *ψ-cryptopine* chloride, in acid solution, is a base,  $C_{21}H_{25}O_4N$ , which is amorphous, but yields a crystalline picrate. Since this base gives 5:6-methylenedioxy-*o*-toluic acid on oxidation with permanganate, it is obvious that its constitution must be represented by the partial formula I, and it has therefore been named *dihydroanhydro-ψ-cryptopine*. The formation of this base is completely analogous to the conversion of *isocryptopine* chloride into *tetrahydroanhydroisocryptopine* (m. p.  $138^\circ$ , p. 722), and the similarity in constitution is clearly exhibited when the partial formulæ are compared:



*Dihydroanhydro-ψ-cryptopine*.



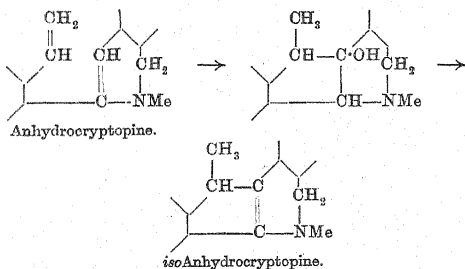
*Tetrahydroanhydroisocryptopine*.

*Section IV (c). The Reduction of  $\psi$ -Methylberberinium Chloride* (p. 778).—In a communication published a short time ago (T., 1918, 113, 750), it was shown that anhydroberberine methosulphate is converted by the action of hydrochloric acid into a substance called  $\psi$ -methylberberinium chloride, which is the analogue in the berberine series of  $\psi$ -cryptopine chloride. Since the latter substance exhibits the abnormal behaviour just described when reduced by sodium amalgam in acid solution, it was thought that it would be interesting to investigate the behaviour of  $\psi$ -methylberberinium chloride in the same circumstances. The strongly acid solution of  $\psi$ -methylberberinium chloride was therefore placed on sodium amalgam, when a neutral substance,  $C_{20}H_{20}O_4$  (*iso- $\psi$ -berberidene*), separated, which melts at  $117^\circ$  and exhibits the closest resemblance to *iso- $\psi$ -cryptopidene*. The main product of the reduction was, however, again a base,  $C_{21}H_{25}O_4N$  (*dihydroanhydro- $\psi$ -methylberberine*), which, although amorphous, yields a crystalline picrate and hydriodide, and obviously corresponds with the amorphous base—dihydroanhydro- $\psi$ -cryptopine—produced during the reduction of  $\psi$ -cryptopine chloride in acid solution.

#### *Section V.*

##### *isoAnhydrocryptopine.*

*isoAnhydrocryptopine* is obtained from anhydrocryptopine by boiling with dilute hydrochloric acid, thus converting it into the isomeric hydroxy*iso*anhydrodihydrocryptopines, and then removing water from the latter by means of phosphoryl chloride (862).

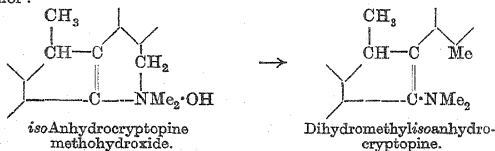


Anhydrocryptopine and *iso*anhydrocryptopine are obviously closely related, since both contain an unsaturated dihydro*iso*-quinoline ring methylated at the nitrogen atom. The behaviour of this ring on reduction has been exhaustively studied in the case

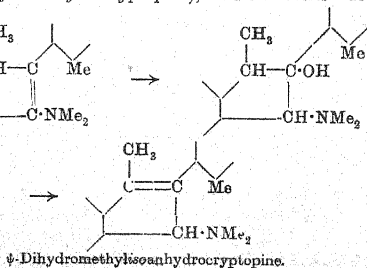
of anhydrocryptopine methosulphate (p. 716), with unexpected results, and it seemed possible that additional information of importance might be obtained if the behaviour of *iso*anhydrocryptopine methosulphate were studied under similar conditions.

To some extent, this expectation was realised, but, on the other hand, wide differences, difficult to understand, were found to occur when the behaviour of the products of reduction obtained in the parallel cases to the subsequent action of reducing agents was investigated.

*Section V (a). The Reduction of isoAnhydrocryptopine Methosulphate in Alkaline Solution* (p. 782).—This methosulphate is readily reduced at the temperature of the steam-bath, when sodium amalgam acts on its aqueous solution, with the separation of a base,  $C_{22}H_{25}O_4N$ , which has been named *dihydromethylisoanhydrocryptopine*. The examination of this base and its derivatives leaves little doubt that its formation is correctly represented in the following manner:



that is to say, it is formed by a process which is analogous to that which occurs when anhydrocryptopine methosulphate is reduced to dihydroanhydromethylcryptopine (p. 716). The new base melts at  $122^\circ$ , and is further characterised by the fact (i) that it exists in well-defined dimorphic modifications (*A*) and (*B*), and (ii) that, on boiling with dilute hydrochloric acid, it undergoes a curious intramolecular change and yields an isomeric base,  $C_{22}H_{25}O_4N$  (*ψ*-*dihydromethylisoanhydrocryptopine*), which melts at  $140^\circ$ .

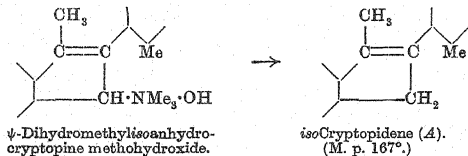


This change is probably due to the addition and subsequent elimination of water, and it is suggested that the process takes place according to the scheme on p. 732.

The occurrence of the grouping,  $\cdot\text{CMe}:\text{C}<$ , receives support from the observation that  $\psi$ -dihydromethylisoanhydrocryptopine is oxidised with unusual difficulty and resists the action of reducing agents in a remarkable degree (p. 788).

The most extraordinary change observed both in the case of dihydromethylisoanhydrocryptopine and its  $\psi$ -isomeride is the behaviour of their methosulphates on reduction in alkaline solution by sodium amalgam.

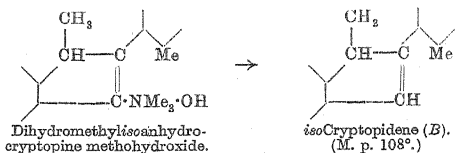
In both cases, trimethylamine is eliminated with great ease, even at the ordinary temperature, and neutral substances,  $\text{C}_{20}\text{H}_{20}\text{O}_4$ , are produced which are isomeric with and somewhat similar in properties to cryptopidene and the  $\psi$ -cryptopidenes (compare pp. 718, 730). Under these conditions, the methosulphate of  $\psi$ -dihydromethylisoanhydrocryptopine (m. p.  $140^\circ$ ) yields, so far as could be ascertained, a single substance—*isocryptopidene* (A)—melting at  $167^\circ$ , and there is reason to believe that this is formed according to the scheme:



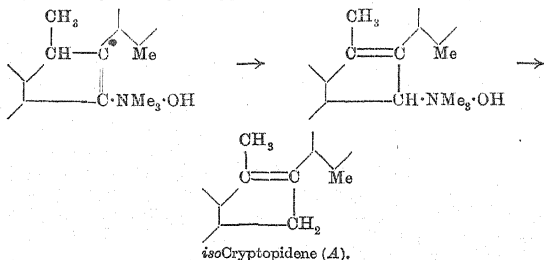
Dihydromethylisoanhydrocryptopine methosulphate behaves in a different manner, yielding two substances,  $\text{C}_{20}\text{H}_{20}\text{O}_4$ , according to the conditions under which the reduction is carried out. If the aqueous solution of the methosulphate is reduced by sodium amalgam at  $30^\circ$ , decomposition takes place very gradually, and the neutral substance which separates melts at  $167^\circ$ , and is identical with the *isocryptopidene* (A) obtained by the reduction of the methosulphate of the  $\psi$ -isomeride. The boiling aqueous solution of the methosulphate of dihydromethylisoanhydrocryptopine is, however, very rapidly decomposed by crushed sodium amalgam, the neutral substance,  $\text{C}_{20}\text{H}_{20}\text{O}_4$ , produced melts at  $108^\circ$ , and is therefore isomeric with *isocryptopidene* (A). It has been named *isocryptopidene* (B).

If an attempt is made to explain this puzzling state of things, it

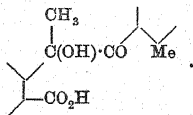
may be suggested that the rapid formation of the substance melting at  $108^{\circ}$  is the direct process,



and that during the slow process at  $30^{\circ}$  the prolonged action of the alkali causes addition and subsequent elimination of water in the direction which is assumed to take place during the conversion of dihydromethylisocyanhydrocryptopine into its  $\psi$ -isomeride (p. 732).



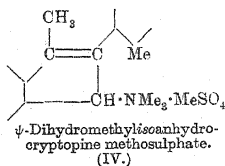
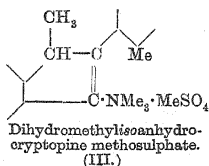
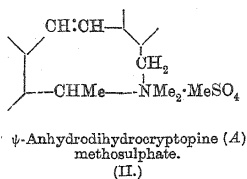
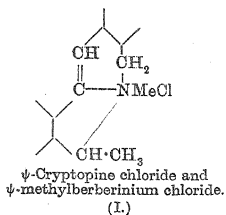
It is, however, obvious that the changes which take place during these eliminations of trimethylamine are most unusual, and explanations of the course which these decompositions take must therefore be considered as merely provisional. Some confirmation of the constitution assigned to isocryptopidene (B) is to be found in its behaviour on oxidation, when it yields a new acid,  $\text{C}_{20}\text{H}_{20}\text{O}_8$  (m. p.  $227^{\circ}$ ), which has been named *ketohydroxydihydroisocryptopidenic acid*, and very probably has the constitution



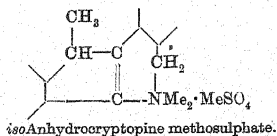
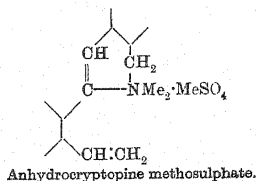
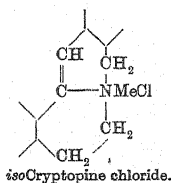
An acid of this constitution could scarcely result from the oxidation of isocryptopidene (A) if the formula assigned to this substance above is correct.

One of the most remarkable decompositions which have been

observed during the course of this long investigation is the process of reduction by sodium amalgam, sometimes in alkaline and sometimes in acid solution, which results in the elimination of the nitrogen atom and separation of a neutral substance,  $C_{20}H_{20}O_4$ . This change has been observed in the following cases:



and the nitrogen atom is eliminated as methylamine in (I), as dimethylamine in (II), and as trimethylamine in (III) and (IV). On the other hand, substances very similar in constitution to those figured above, such, for example, as



do not lose the nitrogen atom when subjected to the action of sodium amalgam under the same conditions.

This matter is obviously very complex and difficult to understand, and, at the present stage, it seems impossible to form any idea as to the conditions which cause the nitrogen atom to be in so reactive a state that it is readily removed by the action of sodium amalgam, sometimes at the ordinary temperature. If opportunity occurs, it is proposed to study the mechanism of changes of this kind in the case of *isoquinoline* derivatives and other analogous substances of less complex structure than the substances discussed in the present communication.

#### EXPERIMENTAL.

##### *Preparation of Anhydrocryptopine Methosulphate,* $C_{21}H_{21}O_4N, Me_2SO_4$ .

It has already been pointed out that the process previously given (978) for the preparation of this substance is unsatisfactory, and, as considerable quantities of this valuable material were required for the purpose of the present investigation, comparative experiments were instituted, and finally the following conditions were found to give a yield of more than 80 per cent. of that theoretically possible.

The anhydrocryptopine employed was prepared from *isocryptopine* chloride substantially according to the method already described (975), but it is not necessary to use more than 20 c.c. of 25 per cent. methyl-alcoholic potassium hydroxide for each 10 grams of the chloride. The product was washed thoroughly at the pump, first with water, then several times with methyl alcohol, in which anhydrocryptopine is very sparingly soluble, and finally with water. The pale yellow product was left in contact with porous porcelain until air-dry, then dried at a temperature not exceeding 80°\* until no further loss in weight occurred; finally, it was powdered and passed through a very fine sieve. Prepared in this way, anhydrocryptopine is nearly pure and melts at about 108—110°; it contains, at the most, traces of inorganic matter and of *isocryptopine* chloride.

In order to prepare the methosulphate, anhydrocryptopine (10 grams) is shaken in a corked flask with excess of freshly distilled

\* If the temperature is allowed to rise to 95—100°, the mass soon becomes brown and viscid and rapidly decomposes, a change which appears to be mainly the result of oxidation. For the successful preparation of the methosulphate, anhydrocryptopine must be quite dry.



methyl sulphate (10 c.c.), when a paste is formed and there is no apparent immediate action. On keeping, the paste rapidly thickens, and in two days will have set to a hard cake. After remaining for four days, the flask is broken, and the cake crushed and washed at the pump with benzene, which removes the excess of methyl sulphate and colouring matter.\*

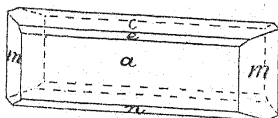
The dry, pale yellow residue is left on porous porcelain until the adherent benzene has evaporated; it then weighs 11 grams, and is dissolved in boiling methyl alcohol, from which the pure methosulphate separates, on slowly cooling, in brilliant sulphur-yellow prisms, and melts at  $238-240^{\circ}$ , as previously stated. The measurement of some fine crystals of anhydrocryptopine methosulphate was kindly undertaken by Miss M. Porter, with the following result:

The crystals are monoclinic with axial ratios  $a:b:c=1.504:1:0.931$ ,  $\beta=104^{\circ}15'$ , the forms observed being  $a\{100\}$ ,  $m\{110\}$ ,  $c\{001\}$ ,  $r\{\bar{1}01\}$ , and  $e\{102\}$ . The habit is tabular parallel to  $c\{001\}$ , and very much elongated along the  $b$ -axis, as shown in Fig. 1. The form  $c\{001\}$  is the predominant terminating form;  $r\{\bar{1}01\}$  is well developed, and  $e\{102\}$ , when present, is very narrow. The crystals gave poor reflections; three were measured, and the results are placed in the table below.

Face.	No. of readings.	Azimuth ( $\phi$ ).			Polar distance ( $\rho$ ).		
		Limits.	Obs.	Calc.	Limits.	Obs.	Calc.
$a$ (100)	4	$89^{\circ}55' - 90^{\circ} 5'$	$90^{\circ} 1'$	$90^{\circ} 0'$	$90^{\circ} 0' - 90^{\circ} 0'$	$90^{\circ} 0'$	$90^{\circ} 0'$
$m$ (110)	4	$34 30 - 34 42$	$*34 34$	—	$90 0 - 90 0$	$90 0$	$90 0$
$c$ (001)	3	$87 25 - 90 35$	$88 47$	$90 0$	$15 48 - 16 2$	$*15 15$	—
$r$ ( $\bar{1}01$ )	3	$87 45 - 90 15$	$89 33$	$90 0$	$19 53 - 20 30$	$*20 15$	—
$e$ (102)	1	—	$90 41$	$90 0$	—	$30 30$	$30 40$

Determinants:  $010/001/100$ . Complex-symbol:  $4h; -15/64\frac{1}{2}/+2$ .

FIG. 1.



\* A quicker process is to dissolve the cake in boiling methyl alcohol, from which the methosulphate separates, on cooling, in an almost pure condition. The yield, however, is not so good as that obtained after extraction with benzene. This is probably due to the fact that the solution in boiling methyl alcohol, containing the excess of methyl sulphate, rapidly becomes very acid, and this causes some decomposition of the methosulphate.

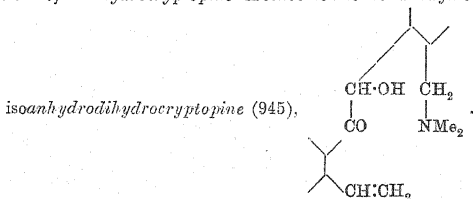
The methyl-alcoholic mother liquors of the pure methosulphate yielded, on concentrating, a further crop of less pure methosulphate, and, on concentrating further and leaving in the ice-chest, a mass of soft, yellow, nearly square plates separated, together with a few of the large prisms of the methosulphate. The two substances were easily separated by means of a sieve, and the second substance, after recrystallisation from water, proved to be *anhydrocryptopine methyle hydrogen sulphate*:

0.1181 gave 0.2471  $\text{CO}_2$  and 0.0582  $\text{H}_2\text{O}$ .  $\text{C}=57.2$ ;  $\text{H}=5.5$ .

$\text{C}_{21}\text{H}_{21}\text{O}_4\text{N}, \text{MeHSO}_4$  requires  $\text{C}=57.0$ ;  $\text{H}=5.4$  per cent.

The most striking difference between the methosulphate and this salt lies in the fact that, whereas the solution of the former gives no precipitate with ammonia, the addition of ammonia to that of the latter causes the immediate separation of a caseous precipitate which, after crystallisation from methyl alcohol, melts at  $110-111^\circ$ , and consists of anhydrocryptopine.

*Oxidation of Anhydrocryptopine Methochloride to Diowymethyl-*



This oxidation was carried out by dissolving anhydrocryptopine methochloride (5 grams; compare 981) in water (1 litre), and, after cooling in ice and salt until the solution was partly frozen, cold saturated permanganate (containing 5.5 grams of  $\text{KMnO}_4$ ) was gradually added with mechanical stirring. The permanganate was immediately decolorised, and, when the operation was complete, the whole was heated to boiling, filtered, and the brown filtrate concentrated to half its bulk, during which a small quantity of a crystalline substance separated. After two days, this was collected (0.5 gram), and a second small quantity was obtained by further concentrating the deep brown filtrate, the total yield being 0.67 gram. On still further concentrating, the odour of dimethylamine became apparent, and all attempts to obtain anything crystalline from the tar which resulted were unsuccessful. The crystalline substance (0.67 gram) is sparingly soluble in cold

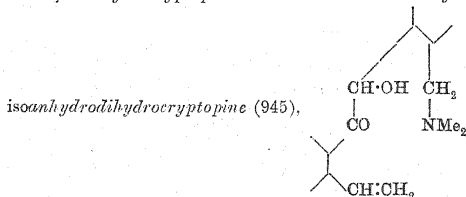
The methyl-alcoholic mother liquors of the pure methosulphate yielded, on concentrating, a further crop of less pure methosulphate, and, on concentrating further and leaving in the ice-chest, a mass of soft, yellow, nearly square plates separated, together with a few of the large prisms of the methosulphate. The two substances were easily separated by means of a sieve, and the second substance, after recrystallisation from water, proved to be *anhydrocryptopine methyl hydrogen sulphate*:

0.1181 gave 0.2471  $\text{CO}_2$  and 0.0582  $\text{H}_2\text{O}$ .  $\text{C}=57.2$ ;  $\text{H}=5.5$ .

$\text{C}_{21}\text{H}_{21}\text{O}_4\text{N}, \text{MeHSO}_4$  requires  $\text{C}=57.0$ ;  $\text{H}=5.4$  per cent.

The most striking difference between the methosulphate and this salt lies in the fact that, whereas the solution of the former gives no precipitate with ammonia, the addition of ammonia to that of the latter causes the immediate separation of a caseous precipitate which, after crystallisation from methyl alcohol, melts at  $110-111^\circ$ , and consists of anhydrocryptopine.

*Oxidation of Anhydrocryptopine Methochloride to Dioxymethyl-*



This oxidation was carried out by dissolving anhydrocryptopine methochloride (5 grams; compare 981) in water (1 litre), and, after cooling in ice and salt until the solution was partly frozen, cold saturated permanganate (containing 5.5 grams of  $\text{KMnO}_4$ ) was gradually added with mechanical stirring. The permanganate was immediately decolorised, and, when the operation was complete, the whole was heated to boiling, filtered, and the brown filtrate concentrated to half its bulk, during which a small quantity of a crystalline substance separated. After two days, this was collected (0.5 gram), and a second small quantity was obtained by further concentrating the deep brown filtrate, the total yield being 0.67 gram. On still further concentrating, the odour of dimethylamine became apparent, and all attempts to obtain anything crystalline from the tar which resulted were unsuccessful. The crystalline substance (0.67 gram) is sparingly soluble in cold

alcohol and not very readily so on boiling, and separates in drab needles. After twice recrystallising, the following analytical details were obtained with different preparations:

0.1129 gave 0.2724  $\text{CO}_2$  and 0.0633  $\text{H}_2\text{O}$ .  $\text{C}=65.8$ ;  $\text{H}=6.2$ .

0.1026 „ 0.2496  $\text{CO}_2$  „ 0.0596  $\text{H}_2\text{O}$ .  $\text{C}=66.3$ ;  $\text{H}=6.4$ .

$\text{C}_{22}\text{H}_{25}\text{O}_6\text{N}$  requires  $\text{C}=66.2$ ;  $\text{H}=6.3$  per cent.

*Dioxymethylisoanhydrodihydrocryptopine* melts at  $187-188^\circ$ , and is sparingly soluble in benzene or acetone in the cold and nearly insoluble in light petroleum. It dissolves in boiling acetone and separates in glistening balls of needles. The substance is a strong base, dissolves immediately in cold dilute hydrochloric acid, and gives, on the addition of ammonia, a milky liquid and an amorphous precipitate which, on warming, becomes crystalline. The sulphate and nitrate, like the hydrochloride, are readily soluble. The addition of platinic chloride to the dilute solution of the hydrochloride produces an ochreous precipitate, which melts to a green oil under boiling water, and the supernatant liquid becomes first green and then brown. Auric chloride produces, with a dilute solution of the hydrochloride, a pale chocolate precipitate, soluble in hot water, and, on boiling, the liquid becomes green and deposits a purple precipitate of reduced gold. When a few drops of copper sulphate are added to the solution of the hydrochloride, a pale yellowish-green solution is obtained which, on boiling, becomes first deep blue, then yellow, and finally deep reddish-brown; the addition of alkali then precipitates a reddish-brown precipitate of cuprous oxide.

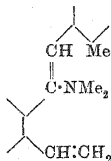
The solution of the base in ordinary dilute nitric acid becomes deep green when heated at about  $80^\circ$ , and is dichroic with a red reflex; if the temperature is raised to the boiling point, the intense colour suddenly changes to pale brown, and the odour of nitrous acid develops.

When concentrated nitric acid is poured on to a trace of the substance on a watch-glass, a brilliant orange-red colour is produced, which soon becomes crimson, and then the addition of water gives a crimson solution, which fades to yellow. The solution of the base in glacial acetic acid gives no immediate coloration on the addition of sulphuric acid, but gradually a pink colour develops. If the base is mixed with acetyl chloride in a sealed tube, it becomes crimson, then violet, and finally intense indigo-blue, and, on heating in boiling water, the colour changes to deep green. The whole dissolves completely in water to a brown solution, and ammonia precipitates a chocolate, gelatinous substance which dries to a chocolate-black powder. The base does not exhibit the characteristic purple benzoin reaction when it is warmed with

dilute sodium hydroxide or boiled with methyl-alcoholic potassium hydroxide, but, in the latter case, it is converted into a white substance, which is apparently a potassium derivative, and this is decomposed by water with the separation of a white, flocculent precipitate.

The base appears to yield a semicarbazone when it is boiled with excess of semicarbazide hydrochloride and sodium acetate and the product precipitated with ammonia, but the amount of available material was too small for purification and analysis.

*Section I (a). Reduction of Anhydrocryptopine Methosulphate in Alkaline Solution: Formation of Dihydroanhydromethylcryptopine,*



Dihydroanhydromethylcryptopine is obtained when anhydrocryptopine methosulphate is reduced in alkaline solution by sodium amalgam under the following conditions: The methosulphate (10 grams), dissolved in boiling water (200 c.c.), was poured on crushed sodium amalgam (100 grams of 4 per cent.) in a porcelain beaker, and the whole vigorously stirred, when a base at once separated which adhered to the sides of the beaker and to the glass rod, and hardened on cooling. The mass was ground up, well washed, dissolved in boiling methyl alcohol, the filtered solution mixed with ether, and the methyl alcohol removed by washing with water. After drying over potassium carbonate, the ethereal solution was concentrated and left for several days in the ice-chest, but, as no crystallisation took place, the ether was evaporated. The hard residue, which resembled colophony, was dissolved in dilute hydrochloric acid and mixed with ammonia, when an amorphous base separated, which was dried over phosphoric oxide in a vacuum desiccator. Two different preparations were analysed:

0.1055 gave 0.2758  $\text{CO}_2$  and 0.0619  $\text{H}_2\text{O}$ .  $\text{C}=71.3$ ;  $\text{H}=6.5$ .

0.1255 „ 0.3312  $\text{CO}_2$  „ 0.0764  $\text{H}_2\text{O}$ .  $\text{C}=71.9$ ;  $\text{H}=6.8$ .

$\text{C}_{22}\text{H}_{25}\text{O}_4\text{N}$  requires  $\text{C}=71.9$ ;  $\text{H}=6.8$  per cent.

*Dihydroanhydromethylcryptopine* exhibits no tendency to crystallise; its solution in acetic acid gives with sulphuric acid a port

wine coloration, which changes to deep brown on the addition of a drop of dilute nitric acid. The salts are readily soluble, and the solution of the hydrochloride gives, on the addition of potassium iodide, a viscid iodide which dissolves readily in methyl alcohol, but could not be obtained crystalline. The *platinichloride*, prepared by the addition of platinic chloride to the dilute solution of the hydrochloride, is a pale ochreous, chalky precipitate:

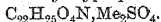
0.1265 gave 0.2146  $\text{CO}_2$  and 0.0516  $\text{H}_2\text{O}$ .  $\text{C}=46.2$ ;  $\text{H}=4.5$ .

$(\text{C}_{22}\text{H}_{25}\text{O}_4\text{N})_2\text{H}_2\text{PtCl}_6$  requires  $\text{C}=46.2$ ;  $\text{H}=4.5$  per cent.

*Oxidation of Dihydroanhydromethylcryptopine*.—In order to obtain evidence as to the constitution of this base, the substance (5 grams), dissolved in acetone, was oxidised by the gradual addition of finely powdered permanganate (5.5 grams) at the ordinary temperature. The product was filtered, the manganese precipitate (A) well washed with acetone, the filtrate evaporated, and the brown syrup, which had a distinct odour of piperonal, distilled in a current of steam. The cloudy distillate deposited, on keeping in the ice-chest, a large crop of needles which melted at  $70-72^\circ$ , and were recognised as 5:6-methylenedioxy-*o*-tolualdehyde (907).

The residue in the steam distillation flask contained an oil, most of which was soluble in dilute hydrochloric acid, but no further examination was made. The manganese precipitate (A) yielded, on extraction with boiling water, a brown solution, which was digested with animal charcoal, concentrated, and acidified, when a solid acid separated and crystallised from glacial acetic acid in colourless needles, melted at  $214-216^\circ$ , and consisted of 5:6-methylenedioxy-*o*-toluic acid (916).

*Dihydroanhydromethylcryptopine Methosulphate,*



The solution of the base (3 grams) in benzene (15 c.c.) reacts readily with methyl sulphate (3 c.c.), with development of heat, and in a short time the methosulphate separates as a crystalline mass. This was collected, washed with benzene, and crystallised from water, in which it is rather sparingly soluble in the cold, but readily so on boiling, and from which it separates in colourless groups of prisms:

0.1164 gave 0.2499  $\text{CO}_2$  and 0.0661  $\text{H}_2\text{O}$ .  $\text{C}=58.5$ ;  $\text{H}=6.3$ .

$\text{C}_{22}\text{H}_{25}\text{O}_4\text{N}, \text{Me}_2\text{SO}_4$  requires  $\text{C}=58.4$ ;  $\text{H}=6.3$  per cent.

This methosulphate melts at  $210^\circ$ , without effervescence, to a slightly coloured syrup; the solution in acetic acid gives with sulphuric acid a deep cherry-red coloration which, on the addition

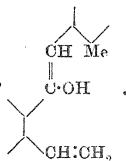
of a drop of dilute nitric acid, changes to brownish-violet. The corresponding *methiodide*,  $C_{22}H_{25}O_4N, MeI$ , is obtained by adding hot dilute potassium iodide to the hot dilute solution of the methosulphate, when a milky liquid is produced, which soon deposits glistening spangles:

0.1123 gave 0.2242  $CO_2$  and 0.0559  $H_2O$ .  $C = 54.4$ ;  $H = 5.5$ .

$C_{22}H_{25}O_4N, MeI$  requires  $C = 54.2$ ;  $H = 5.5$  per cent.

This iodide is remarkably stable, it scarcely darkens at  $200^\circ$ , and melts at about  $217^\circ$  with very little decomposition.

*Hydroxycryptopidene* (compare 926),



This interesting substance, isomeric and closely allied in properties with  $\alpha$ -isocryptopidol (m. p.  $90-92^\circ$ ; 948), is obtained when dihydroanhydromethylcryptopine methosulphate is decomposed by methyl-alcoholic potassium hydroxide. The methosulphate (7 grams), dissolved in hot methyl alcohol, was mixed with methyl-alcoholic potassium hydroxide (60 c.c. of 25 per cent.) and heated to boiling, when trimethylamine was immediately eliminated, but decomposition was nevertheless slow.

After an hour, most of the methyl alcohol was evaporated, and the pasty residue heated in boiling water for two hours; water was then added, and the viscid precipitate extracted with much ether. The ethereal solution, which contained a flocculent precipitate consisting apparently of a polymeric modification of hydroxycryptopidene (compare below), was filtered, thoroughly washed with dilute hydrochloric acid, dried over potassium carbonate, and concentrated, when, on remaining for several days in the ice-chest, a crust of nodules separated which melted at  $88-89^\circ$ , and consisted of pure hydroxycryptopidene. As the amount which had separated was only small, the ethereal mother liquor was evaporated, when a pale brown syrup remained which soon began to crystallise in nodules, and crystallisation was much facilitated by trituration with methyl alcohol, in which the substance is sparingly soluble. After collecting and washing with methyl alcohol, the colourless residue was recrystallised from methyl alcohol, from which hydroxycryptopidene separates in circular nodules melting at  $87-89^\circ$ . Two different preparations were analysed:

0.1272 gave 0.3288  $\text{CO}_2$  and 0.0704  $\text{H}_2\text{O}$ .  $\text{C}=70.4$ ;  $\text{H}=6.1$ .

0.1289 „ 0.3336  $\text{CO}_2$  „ 0.0701  $\text{H}_2\text{O}$ .  $\text{C}=70.5$ ;  $\text{H}=6.1$ .

$\text{C}_{20}\text{H}_{20}\text{O}_5$  requires  $\text{C}=70.6$ ;  $\text{H}=5.9$  per cent.

*Hydroxycryptopidene* is very readily soluble in benzene, but sparingly so in ether or cold, light petroleum. It dissolves, however, moderately readily in the latter solvent on boiling, and separates in well-developed chisel-shaped prisms and also in single lenticular prisms.

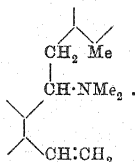
Hydroxycryptopidene dissolves in acetyl chloride in the cold with some development of heat, and, when heated in a sealed tube, the solution becomes purple, then bluish-violet, and finally deep indigo-blue. When the product is evaporated on the steam-bath, a blue resin remains, which loses its colour on boiling with methyl alcohol, and a chalky substance separates. This was collected, washed with methyl alcohol, in which it is nearly insoluble, and purified by dissolving in glacial acetic acid and precipitating with methyl alcohol. After washing with methyl alcohol, the chalky residue contained 4.98 per cent. of chlorine, and this was removed by boiling with 10 per cent. methyl-alcoholic potassium hydroxide. The precipitate was then collected, washed well with methyl alcohol, then with water, dissolved in glacial acetic acid, and precipitated by methyl alcohol:

0.1158 gave 0.3005  $\text{CO}_2$  and 0.0603  $\text{H}_2\text{O}$ .  $\text{C}=70.8$ ;  $\text{H}=5.8$ .

$\text{C}_{20}\text{H}_{20}\text{O}_5$  requires  $\text{C}=70.6$ ;  $\text{H}=5.9$  per cent.

Clearly the action of the acetyl chloride had been, not to produce an acetyl derivative, but to convert the hydroxycryptopidene into a polymeric modification, which, since it closely resembles  $\beta$ -isocryptopidol (947), may be named *hydroxyisocryptopidene* ( $\beta$ ). This polymeride shrinks at  $175$ – $180^\circ$  and froths up at about  $200^\circ$ .

*Section I(b). Reduction of Anhydrocryptopine Methosulphate in Acid Solution: Formation of Tetrahydroanhydromethylcryptopine,*



In preparing tetrahydroanhydromethylcryptopine, anhydrocryptopine methosulphate (5 grams), dissolved in warm water



(100 c.c.) and dilute hydrochloric acid (5 c.c.), was poured on sodium amalgam in a flat basin, and then hydrochloric acid (20 c.c.) gradually added, so that the whole always remained distinctly acid.\* As soon as the amalgam was exhausted, the liquid was filtered from a small quantity of a viscid substance insoluble in dilute hydrochloric acid, mixed with excess of ammonia, and the milky product extracted with ether. The ethereal solution was washed with water, dried over potassium carbonate, and concentrated, and, as no crystallisation had taken place after remaining for a week in the ice-chest, the ether was evaporated. The gummy residue was then dissolved in dilute hydrochloric acid, precipitated by ammonia, and, after collecting and washing, the base was dried in a vacuum desiccator over phosphoric oxide:

0.1140 gave 0.2972  $\text{CO}_2$  and 0.0757  $\text{H}_2\text{O}$ .  $\text{C}=71.1$ ;  $\text{H}=7.4$ .

$\text{C}_{22}\text{H}_{27}\text{O}_4\text{N}$  requires  $\text{C}=71.5$ ;  $\text{H}=7.3$  per cent.

*Tetrahydroanhydromethylcryptopine*, isomeric with anhydrotetrahydromethylcryptopine (m. p.  $107^\circ$ ; 898), has not been obtained in a crystalline condition.

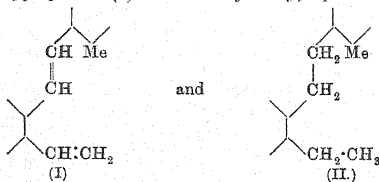
It is readily soluble in dilute hydrochloric acid, and the addition of concentrated hydrochloric acid produces a milky liquid, from which the hydrochloride separates as a syrup. The *platinichloride*, prepared in the usual manner, is an ochreous precipitate somewhat soluble in hot water, from which it separates as a chalky powder:

0.1175 gave 0.1997  $\text{CO}_2$  and 0.0539  $\text{H}_2\text{O}$ .  $\text{C}=46.3$ ;  $\text{H}=5.0$ .

0.4372 „ 0.0719 Pt.  $\text{Pt}=16.4$ .

$(\text{C}_{22}\text{H}_{27}\text{O}_4\text{N})_2, \text{H}_2\text{PtCl}_6$  requires  $\text{C}=46.1$ ;  $\text{H}=5.0$ ;  $\text{Pt}=16.9$  per cent.

*Cryptopidene (I) and Tetrahydrocryptopidene (II),*



The methosulphate of tetrahydroanhydromethylcryptopine does not separate when the solution of the base (2 grams) in benzene

\* It is important that the temperature should not rise above  $60^\circ$ , and that a large excess of hydrochloric acid is not present at any time, otherwise there is a risk of the formation of considerable quantities of  $\psi$ -cryptopine chloride (compare p. 767).

(5 c.c.) is mixed with methyl sulphate (2 c.c.) and allowed to remain for twenty-four hours.

On the addition of ether, the methosulphate is deposited, however, as a syrup, which on rubbing shows signs of crystallising. The syrup was washed with ether, dissolved in a little methyl alcohol, and boiled with methyl-alcoholic potassium hydroxide (20 c.c. of 30 per cent.), when trimethylamine was eliminated, and, after half an hour, the methyl alcohol was evaporated, the residue mixed with water, and extracted with ether. The ethereal solution, which had a lilac fluorescence, after well washing with dilute hydrochloric acid and drying over potassium carbonate, deposited on evaporation a syrup, which soon crystallised, and contact with porous porcelain removed traces of oily impurity. The colourless residue separated from methyl alcohol in glistening needles exhibiting a striking lilac fluorescence, melted at  $122-123^{\circ}$ , and was recognised as *cryptopidine*. The identity was confirmed by analysis (Found: C=73.6; H=6.2.  $C_{20}H_{24}O_4$  requires C=74.1; H=6.2 per cent.) and by the fact that the mixture with a specimen of *cryptopidine* which had previously been obtained from anhydrotetrahydromethylcryptopine methosulphate (926) melted at  $120-122^{\circ}$ .

*Tetrahydrocryptopidine*,  $C_{20}H_{24}O_4$ .—This fine substance is obtained when *cryptopidine* is reduced in boiling alcoholic solution with sodium, but the change does not take place very readily and completely.

The boiling solution of *cryptopidine* (5 grams) in alcohol (100 c.c.) was run on to melted sodium (10 grams) contained in a flask fitted with a long condenser and heated in boiling salt solution. Small quantities of boiling alcohol were run in from time to time, and, so soon as all the sodium had dissolved, water was added, the whole extracted with ether, the ethereal solution washed thoroughly, dried, and evaporated, when a crystalline residue remained, which, however, contained unchanged *cryptopidine*. The reduction was twice repeated exactly as in the first instance, and the product repeatedly recrystallised from methyl alcohol, in which *tetrahydrocryptopidine* is rather sparingly soluble in the cold, and from which it separates in glistening groups of prisms exhibiting a lilac fluorescence. Considerable difficulty was experienced in obtaining accurate analytical results:

0.1236 gave 0.3284  $CO_2$  and 0.0797  $H_2O$ . C=72.6; H=7.2.

0.1142 „ 0.3048  $CO_2$  „ 0.0750  $H_2O$ . C=72.7; H=7.3.

$C_{20}H_{24}O_4$  requires C=73.2; H=7.3 per cent.

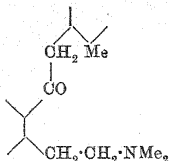
*Tetrahydrocryptopidine* melts at  $78^{\circ}$ , and is readily soluble in

hot alcohol, acetone, acetic acid, or benzene. It is sparingly soluble in light petroleum (b. p. 60—80°) in the cold, but dissolves readily on boiling, and separates splendidly in stout, well-developed tabular prisms with bevelled edges when the solution is allowed to cool very slowly or to concentrate spontaneously. The solution in acetic acid gives with sulphuric acid an orange-red coloration, which changes to a port wine colour on the addition of a drop of dilute nitric acid. It dissolves in concentrated nitric acid with a striking crimson colour, which soon fades.

### Section II.

#### *Reduction of Cryptopine Methochloride in Alkaline Solution.*

*Dihydromethylcryptopine,*



In studying this reduction, the solution of the methochloride (881) (5 grams) in water (100 c.c.) was treated at about 50° with sodium amalgam (100 grams of 4 per cent.), when rapid separation of a viscid, grey base occurred, and the completion of the process was facilitated by heating on the steam-bath. The base was dissolved in methyl alcohol, mixed with much ether, the ethereal solution thoroughly washed with water, dried over potassium carbonate, and concentrated, when, on keeping in the ice-chest, a hard crust of rather indefinite crystals gradually separated, which melted at about 100—102°. The crystals were again dissolved in dry ether, by the aid of methyl alcohol as before, and the rather concentrated liquid then deposited a small quantity of glistening, prismatic needles (0.2 gram) of dihydromethylcryptopine, which became opaque on drying in the steam-oven:

0.1184 gave 0.2977 CO<sub>2</sub> and 0.0757 H<sub>2</sub>O. C=68.6; H=7.1.

C<sub>22</sub>H<sub>27</sub>O<sub>6</sub>N requires C=68.6; H=7.0 per cent.

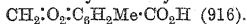
*Dihydromethylcryptopine* melts at 118—120°, and is readily soluble in hot methyl alcohol, but sparingly so in the cold, separating from the hot solution on slowly cooling in glistening, six-sided prisms. When triturated with dilute hydrochloric acid, the base at first becomes viscid, and then the very sparingly soluble hydrochloride forms, which dissolves in boiling dilute hydrochloric

acid and separates as a crust of microscopic prisms. The solution of a trace of the base in a drop of glacial acetic acid gives, with sulphuric acid, a deep reddish-brown coloration.

*Oxidation.*—The base (0.7 gram), dissolved in acetone (20 c.c.), was oxidised by the gradual addition of very finely powdered permanganate (1.2 grams), but the reduction of the permanganate took place unusually slowly and required two days for completion at the ordinary temperature.

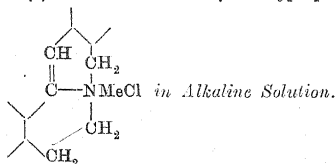
After filtering and washing with acetone, the manganese precipitate was extracted with boiling water, the extract digested with animal charcoal, evaporated to a small bulk, and acidified, when a cloudy liquid was produced, which soon deposited a sparingly soluble, crystalline acid.

This was collected and recrystallised from glacial acetic acid, when it separated in colourless needles melting at 214—216°, which were recognised as 5:6-methylenedioxy-*o*-toluic acid,



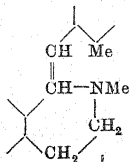
The acetone extract from the oxidation was scarcely coloured, and yielded, on evaporation, a syrup which had the odour of piperonal, and was largely insoluble in dilute hydrochloric acid. On distilling in a current of steam, there separated from the distillate needles which melted at 72—73°, and consisted of 5:6-methylenedioxy-*o*-tolualdehyde,  $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_2\text{Me}\cdot\text{CHO}$  (907).

The ethereal mother liquors from which the dihydromethylcryptopine had separated, as explained above, were concentrated and left for some days in the ice-chest; the hard cake of crystals was then dissolved in dilute hydrochloric acid, and again allowed to remain, when a crust of crystals (0.8 gram) of anhydrotetrahydromethylcryptopine hydrochloride,  $\text{C}_{22}\text{H}_{27}\text{O}_4\text{N}\cdot\text{HCl}$  (900), separated. This sparingly soluble hydrochloride was removed by filtration, the filtrate made strongly alkaline with ammonia, and the viscid base extracted with ether. After drying over potassium carbonate and concentrating, the ethereal solution deposited hard crystals which melted at 106—107°, and consisted of tetrahydromethylcryptopine,  $\text{C}_{22}\text{H}_{29}\text{O}_5\text{N}$  (896). The latter is the principal product of the reduction of cryptopine methochloride under the conditions described at the beginning of this section. Experiments were also made on the reduction of cryptopine methosulphate (880) in alkaline solution with sodium amalgam, but the only product that could be isolated was tetrahydromethylcryptopine.

Section III (a). The Reduction of *isocryptopine Chloride*,

For the purpose of this investigation, crushed sodium amalgam (100 grams of 4 per cent.) was added to *isocryptopine chloride* (5 grams), dissolved in about 400 c.c. of boiling water, and the whole placed on the steam-bath and well stirred, the water being replaced as it evaporated.

A viscid base soon began to separate, and, after an hour, the whole was filtered hot and the residue washed with hot water. The filtrate, mixed with excess of hydrochloric acid, deposited a large quantity of a quaternary salt, which was readily recognised as *isodihydrocryptopine*  $\beta$ -chloride (compare p. 721), and this substance is produced in such considerable amount that this process affords a much more convenient means for its preparation than that previously described (934). The viscid base was dissolved in alcohol and mixed with much ether, which caused a further small quantity of the quaternary salt to separate; this was filtered off, the ethereal solution washed thoroughly until free from alcohol, quickly dried over potassium carbonate, and filtered. During the subsequent concentration, a base began to separate on the sides of the flask as a glistening, crystalline crust, and, on long keeping in the ice-chest, this increased considerably. When this deposit was fractionally crystallised from methyl alcohol, it separated into (i) considerable quantities of *tetrahydroanhydroisocryptopine*,  $C_{21}H_{25}O_4N$  (m. p.  $138^\circ$ ), identical with the base obtained as one of the products of the reduction of *isocryptopine chloride* in acid solution (p. 751), and quite small quantities of a new base,  $C_{21}H_{23}O_4N$ —*dihydroanhydroisocryptopine*—melting at  $195^\circ$ , the constitution of which is represented by the formula



0.0829 gave 0.2174  $\text{CO}_2$  and 0.0480  $\text{H}_2\text{O}$ .  $\text{C}=71.5$ ;  $\text{H}=6.4$ .

0.1246 „ 0.3261  $\text{CO}_2$  „ 0.0729  $\text{H}_2\text{O}$ .  $\text{C}=71.4$ ;  $\text{H}=6.5$ .

$\text{C}_{21}\text{H}_{23}\text{O}_4\text{N}$  requires  $\text{C}=71.4$ ;  $\text{H}=6.5$  per cent.

This interesting substance separates from alcohol or methyl alcohol, in both of which it is very sparingly soluble, in pale lemon-yellow needles.

It is also sparingly soluble in boiling benzene or acetone, and separates particularly well from the latter in glistening needles. The solution in glacial acetic acid gives no coloration with sulphuric acid but, on the addition of a drop of dilute nitric acid, an intense permanganate coloration rapidly develops.

*The Hydrochloride.*—The base dissolves readily in dilute hydrochloric acid, and, on rubbing, the hydrochloride soon separates in needles. It is readily soluble in boiling water, but almost insoluble in dilute hydrochloric acid in the cold:

0.1151 gave 0.2721  $\text{CO}_2$  and 0.0652  $\text{H}_2\text{O}$ .  $\text{C}=64.5$ ;  $\text{H}=6.3$ .

$\text{C}_{21}\text{H}_{23}\text{O}_4\text{N}, \text{HCl}$  requires  $\text{C}=74.7$ ;  $\text{H}=6.2$  per cent.

The sulphate is soluble and does not appear to crystallise readily, but the addition of nitric acid to the dilute solution of the sulphate immediately precipitates the nitrate, which is very sparingly soluble in hot dilute nitric acid and crystallises rather indefinitely. When boiling dilute potassium iodide is added to the boiling dilute solution of the sulphate, a milky liquid is produced, from which the *hydriodide* soon separates as a crystalline mass. This was collected and recrystallised from boiling alcohol, in which the salt is sparingly soluble and from which it separates in warty aggregates melting at about  $250-255^\circ$  with decomposition to a yellow froth:

0.1046 gave 0.2017  $\text{CO}_2$  and 0.0471  $\text{H}_2\text{O}$ .  $\text{C}=52.6$ ;  $\text{H}=5.0$ .

$\text{C}_{21}\text{H}_{23}\text{O}_4\text{N}, \text{HI}$  requires  $\text{C}=52.4$ ;  $\text{H}=5.0$  per cent.

### *Section III (b). The Reduction of isoCryptopine Chloride in Acid Solution.*

In attempting this reduction, considerable difficulty was experienced owing to the sparing solubility of *isocryptopine* chloride in dilute hydrochloric acid, and, indeed, in mineral acids in general.

Ultimately, however, the following process was found to work well.

*isocryptopine* chloride (5 grams), dissolved in glacial acetic acid (25 c.c.), is mixed with boiling water (100 c.c.), and, after heating to boiling, concentrated hydrochloric acid (20 c.c.) is added, and the whole poured on sodium amalgam (100 grams of 4 per

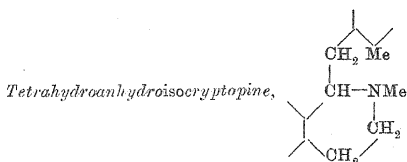
cent.) in an enamelled iron basin. So soon as the vigorous action has subsided, the same quantity of sodium amalgam is again added, as well as sufficient hydrochloric acid to keep the liquid strongly acid. The whole while hot is decanted from the mercury on to a Büchner funnel connected with the pump, and the filtrate, which immediately begins to crystallise in minute needles, left overnight.

The precipitate (*A*) is collected, washed with a little water, the filtrate heated to boiling and mixed with excess of ammonia, when a viscid, grey mass (*B*) separates, which is immediately filtered off, and the filtrate, on keeping overnight, becomes filled with a soft mass of needles (*C*). The substance (*A*), which is almost pure *isocryptopine* chloride, is again reduced as before, and, even after the operation has been repeated four times, *isocryptopine* chloride still remains.

This was proved by analysis (Found: C=59.3; H=6.3.  $C_{21}H_{22}O_4NCl \cdot 2H_2O$  requires C=59.5; H=6.1 per cent.) and also by the fact that the salt yielded anhydrocryptopine (975) on decomposition with methyl-alcoholic potassium hydroxide. The quaternary salt (*C*) crystallised well from hot dilute hydrochloric acid in long needles, and, in contact with porous porcelain, dried to a horny mass which did not melt at 260°. On examination, this salt was found to be *isodihydrocryptopine*  $\beta$ -chloride, since, when digested with methyl-alcoholic potassium hydroxide, it yielded a substance which, after crystallisation from acetone, melted at 178°, and was recognised as anhydrodihydrocryptopine (*A*) (938).

The viscid, grey mass (*B*) hardens on keeping, and becomes crystalline in contact with methyl alcohol. The whole is dissolved in boiling methyl alcohol and set aside, when a crop of crystals separates which usually consists of a mixture of *tetrahydroanhydroisocryptopine* (m. p. 138°) and *dihydroanhydrodihydrocryptopine* (*A*) (m. p. 164°).

The latter of these is much the less soluble in methyl alcohol, and at some concentrations separates almost completely before the base, melting at 138°, begins to crystallise. If this is not the case, fractional crystallisation from methyl alcohol must be resorted to until separation is complete. The constitutional formulæ of the two bases and their derivatives are discussed fully in the introduction (pp. 722 and 723).



This base, obtained as described in the last section, separates from methyl alcohol in groups of striated, prismatic needles, and melts at 138—139°:

0.1139 gave 0.2958 CO<sub>2</sub> and 0.0731 H<sub>2</sub>O. C=70.8; H=7.1.

0.1253 „ 0.3264 CO<sub>2</sub> „ 0.0804 H<sub>2</sub>O. C=71.0; H=7.1.

C<sub>21</sub>H<sub>25</sub>O<sub>4</sub>N requires C=71.0; H=7.0 per cent.

*Tetrahydroanhydroisocryptopine* is readily soluble in boiling alcohol, acetone, or benzene, and crystallises well from all these solvents. Discoloured specimens of the base are readily purified by dissolving in dilute hydrochloric acid, digesting with animal charcoal, and precipitating with ammonia. In this condition, the base is soluble in ether, and the ethereal solution, after drying over potassium carbonate and concentrating, deposits the base as a colourless, crystalline crust.

The *salts* with mineral acids are readily soluble, and crystallise from concentrated solutions in needles. Long boiling with concentrated hydrochloric acid does not appear to have any action on the hydrochloride, which separates, on keeping in the ice-chest, in balls of needles. The solution of a crystal of the base in acetic acid gives with sulphuric acid a pale brown coloration, which becomes greenish-brown on keeping, and the addition of a drop of dilute nitric acid changes the colour to deep port wine. The *platinichloride* is obtained, on the addition of platinic chloride to the dilute solution of the hydrochloride, as a pale yellow, caseous precipitate, which soon becomes crystalline. It dissolves appreciably in boiling water, and separates as a heavy, pale orange deposit consisting of groups of irregular plates:

0.1272 gave 0.2069 CO<sub>2</sub> and 0.0507 H<sub>2</sub>O. C=44.4; H=4.5.

0.5064 „ 0.0854 Pt. Pt=16.9.

(C<sub>21</sub>H<sub>25</sub>O<sub>4</sub>N)<sub>2</sub>.H<sub>2</sub>PtCl<sub>6</sub> requires C=45.0; H=4.6; N=17.3 per cent.

The mercurichloride separates, on adding mercuric chloride to the dilute solution of the hydrochloride, as a white, caseous precipitate which soon becomes crystalline; it melts under boiling water, dissolves moderately readily, and, when cooled and rubbed, the milky liquid soon crystallises.



*The Methosulphate.*—This derivative is readily obtained by adding methyl sulphate (1 c.c.) to the solution of the base (1 gram) in warm benzene, when there is appreciable development of heat, but no immediate separation.\* On keeping in the ice-chest, glistening plates soon begin to form, and, after twenty-four hours, the substance is collected and washed with benzene, but it was not recrystallised, because it is very readily soluble both in water and in methyl alcohol.

After drying in the steam-oven, it softened at  $145^{\circ}$  and melted at about  $160^{\circ}$ :

0.1185 gave 0.2509  $\text{CO}_2$  and 0.0686  $\text{H}_2\text{O}$ .  $\text{C}=57.7$ ;  $\text{H}=6.4$ .

$\text{C}_{21}\text{H}_{25}\text{O}_4\text{N}, \text{Me}_2\text{SO}_4$  requires  $\text{C}=57.4$ ;  $\text{H}=6.5$  per cent.

The aqueous solution of this methosulphate gave no precipitate on the addition of ammonia or dilute sodium hydroxide.

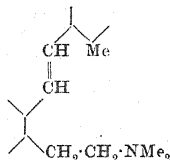
*The Methiodide.*—The addition of hot dilute potassium iodide to the hot aqueous solution of the methosulphate produces a milky liquid, which soon crystallises beautifully in glistening scales:

0.1124 gave 0.2179  $\text{CO}_2$  and 0.0565  $\text{H}_2\text{O}$ .  $\text{C}=52.7$ ;  $\text{H}=5.6$ .

$\text{C}_{21}\text{H}_{25}\text{O}_4\text{N}^{\oplus}\text{MeI}$  requires  $\text{C}=53.1$ ;  $\text{H}=5.6$  per cent.

This methiodide does not become yellow until about  $250^{\circ}$ , and melts at about  $263^{\circ}$ , without effervescence, to a lemon-yellow liquid. It is very sparingly soluble in water or alcohol, and separates, when the solution in the latter solvent is concentrated, as a glistening, heavy powder consisting of stout prisms with bevelled edges.

*Anhydrotetrahydromethylcryptopine,*



This substance is produced when the methosulphate of tetrahydroanhydroisocryptopine is decomposed by methyl-alcoholic potassium hydroxide. The methosulphate (1 gram) was boiled with methyl-alcoholic potassium hydroxide (10 c.c. of 20 per cent.) in an open flask for ten minutes, when decomposition set in readily and a cloudy liquid was produced, which soon deposited a white, crystalline precipitate. The product was mixed with water, heated

\* If, however, the benzene solution is boiling, a vigorous reaction sets in, and the methosulphate commences to crystallise at once, the separation being complete in a few minutes.

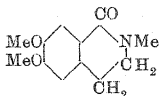
to boiling, the aqueous liquid decanted from the viscid mass, and the latter recrystallised from methyl alcohol, from which it separated in glistening, colourless plates having a striking lilac fluorescence and melting at 107—109°. That this substance was anhydrotetrahydromethylcryptopine was proved by analysis (Found: C=71.2; H=7.3; N=3.9.  $C_{22}H_{27}O_4N$  requires C=71.5; H=7.3; N=3.8 per cent.) and by the fact that a mixture of the substance with a specimen of anhydrotetrahydromethylcryptopine which had been prepared from tetrahydromethylcryptopine (899) melted at 106—108°. Moreover, a comparison of the crystals clearly established the identity of the two preparations.

*Oxidation of Tetrahydroanhydroisocryptopine.*—This oxidation, which has afforded valuable evidence in support of the constitution assigned to the above substance (p. 751), was carried out under the following conditions. The base (9 grams) was dissolved in warm acetone (400 c.c.), the solution cooled to the ordinary temperature, and then very finely powdered and sieved permanganate (13 grams) added in small quantities at a time with vigorous stirring. Oxidation was slow at first, but became more rapid as the temperature rose, and care was taken that the temperature remained below 20° throughout the operation. The product was filtered, the manganese precipitate thoroughly washed with acetone, and the acetone filtrate treated as described below.

When the manganese precipitate was extracted with boiling water, a very slightly coloured filtrate was obtained which, after concentrating considerably, yielded, on acidifying with hydrochloric acid, a very sparingly soluble, nearly colourless, chalky precipitate (2 grams). This was collected and crystallised from glacial acetic acid, from which it separated in needles melting at 215—216°, and yielded on analysis: C=60.0; H=4.6, whereas  $C_9H_8O_4$  requires C=60.0; H=4.5 per cent. Careful comparison showed that this acid was identical with 5:6-methylenedioxy-*o*-toluic acid (916),  $CH_2:O_2:C_6H_2Me.CO_2H$ .

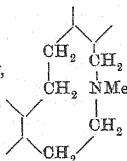
The acetone solution, which had been filtered from the manganese precipitate as described above, was evaporated, when a yellow syrup remained, which gradually deposited needle-shaped crystals. When the whole was distilled in a current of steam, a milky distillate was obtained, which deposited a mass of crystals having the odour of piperonal, and, after recrystallisation from light petroleum, melted at 73—74°. That this substance was 5:6-methylenedioxy-*o*-tolualdehyde,  $CH_2:O_2:C_6H_2Me.CHO$ , was proved by direct comparison with a specimen of this substance which had previously been obtained by the oxidation of anhydrotetrahydromethylcryptopine (907). The residue in the steam dis-

tillation flask was extracted with ether, the ethereal solution washed with very dilute hydrochloric acid to remove any basic substances, dried over potassium carbonate, and evaporated. When the residual, pale yellow syrup was seeded with a trace of 1-keto-6:7-dimethoxy-2-methyltetrahydroisoquinoline,



(m. p.  $126^{\circ}$ ) (Pyman, T., 1909, **95**, 1272; 1910, **97**, 269), it rapidly became crystalline. After remaining in contact with porous porcelain for a couple of days, the colourless, crystalline residue was recrystallised from dry ether, from which it separated in prisms melting at  $126^{\circ}$ . Moreover, the intimate mixture with a specimen, prepared by the method described by Pyman, melted at the same temperature.

*Dihydroanhydrodihydrocryptopine (A),*



This base, produced by the reduction of *isocryptopine* chloride under the conditions specified on p. 750, separates from acetone, in which it is rather sparingly soluble, in groups of glistening prisms, and melts at  $163$ — $164^{\circ}$ :

0.1057 gave 0.2752  $\text{CO}_2$  and 0.0670  $\text{H}_2\text{O}$ .  $\text{C}=71.0$ ;  $\text{H}=7.0$ .

0.1036 „ 0.2701  $\text{CO}_2$  „ 0.0661  $\text{H}_2\text{O}$ .  $\text{C}=71.1$ ;  $\text{H}=7.1$ .

$\text{C}_{21}\text{H}_{25}\text{O}_4\text{N}$  requires  $\text{C}=71.0$ ;  $\text{H}=7.0$  per cent.

*Dihydroanhydrodihydrocryptopine (A)* is characterised by being remarkably sparingly soluble in boiling methyl alcohol, from which it separates in stars of flat needles; it is much more readily soluble in ethyl alcohol, and readily so in benzene. The solution of a crystal in a drop of acetic acid yields, on mixing with sulphuric acid, at first no coloration, but gradually an intense indigo develops, and the addition of a drop of dilute nitric acid changes this to orange.

The salts of dihydroanhydrodihydrocryptopine (*A*) are much less readily soluble in water or dilute acids than those of the isomeric

tetrahydroanhydroisocryptopine (p. 751). When dilute hydrochloric acid is added to the base, the crystals at first dissolve, but almost at once the hydrochloride commences to separate, and is very sparingly soluble in cold dilute hydrochloric acid. It dissolves readily, however, on boiling, and separates in groups of flat needles. The sulphate is also sparingly soluble in dilute sulphuric acid, and crystallises in long hairs radiating from a centre. The base does not dissolve in dilute nitric acid, but is at once converted into the crystalline nitrate, which is more sparingly soluble than either the hydrochloride or sulphate, and separates from its solution in hot dilute nitric acid in stout, prismatic needles with bevelled edges. When boiling dilute solutions of the hydrochloride and potassium iodide are mixed, a clear solution is formed, from which the hydriodide separates in stars of thin laminæ, and is almost insoluble in cold water. The *platinichloride* separates, on the addition of platinic chloride to a hot dilute solution of the hydrochloride, as a viscid, pale ochreous precipitate, which soon hardens; it is somewhat soluble in boiling water and crystallises in microscopic balls of needles:

0.1130 gave 0.1848  $\text{CO}_2$  and 0.0464  $\text{H}_2\text{O}$ .  $\text{C}=44.6$ ;  $\text{H}=4.6$ .

0.5052 „ 0.0859 Pt.  $\text{Pt}=17.0$ .

$(\text{C}_{21}\text{H}_{25}\text{O}_4\text{N})_2 \cdot \text{H}_2\text{PtCl}_6$  requires  $\text{C}=45.0$ ;  $\text{H}=4.6$ ;  $\text{Pt}=17.3$  per cent.

The addition of mercuric chloride to the dilute solution of the hydrochloride produces a curdy precipitate resembling silver chloride; this is somewhat soluble in boiling water and separates in stars of prisms.

The picrate is a chrome-yellow precipitate which melts under boiling water and dissolves with difficulty.

*The Methosulphate*.—When methyl sulphate (1 c.c.) is added to the solution of the base (1 gram) in benzene (10 c.c.), there is no separation at first, but, in a minute or two, the liquid clouds and a viscid syrup is deposited which crystallises on rubbing, the whole becoming a glutinous mass of soft needles. The substance is rather difficult to collect, and is so readily soluble in water or methyl alcohol that it could not be recrystallised. After drying in the steam-oven, it yielded the following analysis:

0.1191 gave 0.2499  $\text{CO}_2$  and 0.0701  $\text{H}_2\text{O}$ .  $\text{C}=57.2$ ;  $\text{H}=6.6$ .

$\text{C}_{21}\text{H}_{25}\text{O}_4\text{N} \cdot \text{Me}_2\text{SO}_4$  requires  $\text{C}=57.4$ ;  $\text{H}=6.5$  per cent.

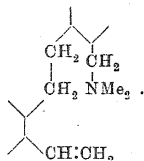
The aqueous solution of this methosulphate gives no precipitate on the addition of ammonia, and a trace of the salt, dissolved in glacial acetic acid, gives no characteristic coloration on the addition of sulphuric acid.

It is mentioned in the introduction (p. 723) that dihydroanhydro-

dihydrocryptopine (A) is unusually resistant towards permanganate, and this was evidenced by the following experiment. A few milligrams of very finely powdered permanganate were added to the solution of the base (3 grams) in acetone (150 c.c.), but no appreciable oxidation had taken place after remaining at 0° for fifteen minutes. When the temperature was raised to 20°, oxidation took place more rapidly, and, after 5 grams of permanganate had been reduced, the product, worked up in the usual manner, yielded 0.175 gram of unchanged base. A small quantity of a resinous, sparingly soluble acid was produced, and also an oily base, but the quantities of these were quite insufficient for further investigation.

*Reduction of Anhydrodihydrocryptopine (A, 938) to Dihydroanhydrodihydrocryptopine (A).*—This conversion, which affords welcome confirmation of the constitution assigned to the last-named substance (p. 723), was carried out under the following conditions: Anhydrodihydrocryptopine (A) (m. p. 178°; 7 grams), dissolved in boiling water and concentrated hydrochloric acid (50 c.c.), was poured on freshly prepared 4 per cent. sodium amalgam (350 grams) in an enamelled iron basin, and the whole well stirred until the amalgam had been completely used. The product contained a colourless, satiny mass of needles, and enough boiling water was added to bring the whole into solution. After filtering, excess of ammonia was added, when a caseous mass separated, which was washed with a little cold water and digested with boiling water to dissolve out a quaternary salt which was present (see below). The residue was dissolved in boiling methyl alcohol, when, on keeping, glistening crystals separated which melted at 162—163°, and consisted of dihydroanhydrodihydrocryptopine (A), since the admixture with a specimen of this substance which had been prepared by the method described at the commencement of this section melted at 162—164°. The identity was confirmed by analysis. The aqueous ammoniacal filtrate from the base (A) deposited, on keeping, a considerable crop of a quaternary salt as a satiny mass of needles. This was collected and identified as isodihydrocryptopine  $\beta$ -chloride (934), since it did not melt at 260°, and, when digested with methyl-alcoholic potassium hydroxide, yielded anhydrodihydrocryptopine (A), melting at 178°.

*Dihydroisoanhydrodihydromethylcryptopine,*



This beautiful substance is obtained when the methosulphate of dihydroanhydrodihydrocryptopine (4) is digested with methyl-alcoholic potassium hydroxide. The methosulphate (3 grams) was dissolved in hot methyl alcohol (25 c.c.), mixed with methyl-alcoholic potassium hydroxide (20 c.c. of 20 per cent.), and heated to boiling in an open flask in such a way that there was considerable concentration. The decomposition took place rather slowly, and, after fifteen minutes, the cloudy solution was mixed with water, when a gum separated which showed no signs of crystallisation on rubbing with methyl alcohol. The whole was extracted with pure ether, the ethereal solution carefully washed, dried over potassium carbonate, concentrated, and left in the ice-chest in a corked flask. For some days nothing separated, and then gradually splendid hard, colourless, brilliant prisms began to form, and increased considerably during three weeks:

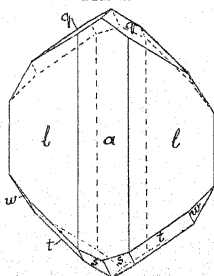
0.1106 gave 0.2890  $\text{CO}_2$  and 0.0730  $\text{H}_2\text{O}$ .  $\text{C}=71.2$ ;  $\text{H}=7.3$ .

0.1215 „ 0.3191  $\text{CO}_2$  „ 0.0803  $\text{H}_2\text{O}$ .  $\text{C}=71.5$ ;  $\text{H}=7.4$ .

$\text{C}_{22}\text{H}_{27}\text{O}_4\text{N}$  requires  $\text{C}=71.5$ ;  $\text{H}=7.3$  per cent.

*Dihydroisoanhydrodihydromethylcryptopine* melts at  $75-77^\circ$ , and is very readily soluble in the usual solvents. The crystals have been examined by Miss M. W. Porter, with the following results:

FIG. 2.



*Dihydroisoanhydrodihydromethylcryptopine.*

The substance is monoclinic with axial ratios  $a:b:c=0.6657:1:0.6899$ ,  $\beta=99^{\circ}34'$ . The forms observed are:  $a(100)$ ,  $l(210)$ ,  $q(011)$ ,  $s(212)$ ,  $t(232)$ ,  $w(\bar{1}21)$ , and, very rarely,  $b(010)$ , which accordingly is not shown in Fig. 2. Three crystals were measured on the two-circle goniometer, and the mean measured and calculated results are given below:

Face.	No. of readings.	$\phi$ (Azimuth).		$\rho$ (Polar distance).	
		Obs.	Calc.	Obs.	Calc.
<i>a</i> (100)	6	90° 9'	90° 0'	90° 0'	90° 0'
<i>b</i> (010)	1	359 29	0 0	90 0	90 0
<i>l</i> (210)	7	*71 50	—	90 0	90 0
<i>q</i> (011)	3	*13 43	—	*35 23	—
<i>s</i> (212)	2	292 0	291 32	42 57	42 13
<i>t</i> (232)	6	320 1	319 49	53 10	53 33
<i>w</i> (121)	4	329 10	327 39	58 47	58 31

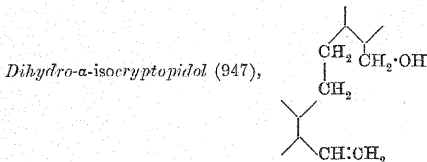
The salts of this base are very readily soluble in water and show little tendency to crystallise. The *platinichloride* was obtained as a pale salmon, chalky precipitate on adding platinic chloride to the dilute solution of the hydrochloride:

0.1171 gave 0.1981  $\text{CO}_2$  and 0.0518  $\text{H}_2\text{O}$ . C=46.2; H=4.9.

0.2028 „ 0.0339 Pt. Pt=16.7.

$(C_{99}H_{27}O_4N)_2 \cdot H_2PtCl_6$  requires C=46.0; H=4.9; Pt=16.9 per cent.

The solution of a crystal of the base in glacial acetic acid gives, with sulphuric acid, a feeble brown coloration, and the addition of a drop of dilute nitric acid changes this to intense port wine. The methosulphate is obtained by adding methyl sulphate (1 c.c.) to the solution of the base (1 gram) in benzene (5 c.c.), when there is distinct rise of temperature and a syrup separates, which gradually crystallises, especially when triturated with ether. This substance is so readily soluble and so badly characterised that no attempt was made to purify it for the purpose of analysis. Its aqueous solution gives no precipitate on the addition of ammonia.



This unsatisfactory substance is obtained from the methosulphate of dihydroisoanhydrodihydromethylcryptopine by the action of methyl-alcoholic potassium hydroxide, trimethylamine being eliminated.

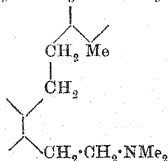
The methosulphate (3 grams), dissolved in a little methyl alcohol, was digested with methyl-alcoholic potassium hydroxide (30 c.c. of 25 per cent.) in an open flask heated just to boiling by means of a salt-solution bath for an hour, the temperature then being raised so that most of the methyl alcohol distilled away and there was no further development of trimethylamine. The residue was mixed with water, the viscid precipitate dissolved in methyl alcohol, mixed with much ether, and the ethereal solution washed with water until quite free from methyl alcohol. After drying over potassium carbonate and concentrating to a small bulk, nothing separated on keeping in the ice-chest for three weeks. The solution was therefore evaporated, when a colourless syrup remained which gradually crystallised, and the buttery mass was left in contact with porous porcelain until dry, but owing to the fact that the substance is so unusually readily soluble in the ordinary solvents and exhibits so little tendency to crystallise, no further purification was possible. After remaining over phosphoric oxide in a vacuum desiccator for a week, the following results were obtained on analysis:

0.1255 gave 0.3201  $\text{CO}_2$  and 0.0798  $\text{H}_2\text{O}$ .  $\text{C}=69.6$ ;  $\text{H}=6.8$ .

$\text{C}_{20}\text{H}_{22}\text{O}_6$  requires  $\text{C}=70.2$ ;  $\text{H}=6.4$  per cent.

This result, coupled with its method of formation, clearly indicates that this substance is *dihydro- $\alpha$ -isocryptidol*.

*Section III (v). Dihydroanhydrotetrahydromethylcryptopine,*



As explained on p. 725, this substance is obtained when the methosulphate either of tetrahydroanhydroisocryptopine (m. p.  $138^\circ$ , p. 752) or dihydroanhydrodihydrocryptopine (A) (m. p.  $164^\circ$ , p. 755) is reduced in alkaline solution by sodium amalgam.

(i) *Reduction of the Methosulphate of Tetrahydroanhydroisocryptopine.*

The solution of this substance (3 grams) in hot water (150 c.c.) is reduced only with considerable difficulty by sodium amalgam (150 grams of 3 per cent.) even on the steam-bath, but a colour-



less oil gradually separates. After the action had proceeded for two hours, the product was left in the ice-chest, when the oil solidified. The mass was well washed and dissolved in hot dilute hydrochloric acid, when, on cooling to  $0^{\circ}$  and rubbing, the hydrochloride separated as a voluminous mass of needles. This salt, which is very sparingly soluble in dilute hydrochloric acid, but readily so in water, was collected, washed with dilute hydrochloric acid, the cold aqueous solution mixed with ammonia, and the milky liquid extracted with ether. The ethereal solution, dried over potassium carbonate and concentrated, did not yield any crystals on remaining in the ice-chest for a week, but on evaporating off the ether, the residual, colourless syrup suddenly crystallised in balls of needles. After leaving in contact with porous porcelain until traces of oily impurity had been absorbed, the colourless, crystalline residue was dissolved in methyl alcohol, in which it is very readily soluble, and the solution allowed to concentrate nearly to dryness over sulphuric acid in a vacuum desiccator. The mass of plates which separated was drained on porous porcelain and recrystallised from a very small quantity of light petroleum, in which the base is very readily soluble.

(ii) *Reduction of the Methosulphate of Dihydroanhydrodihydrocryptopine (A).*

This process was carried out exactly as described under (i), when it was noticed that in the present case the oily base began to separate the moment the hot aqueous solution of the methosulphate was poured on the crushed sodium amalgam. The method of extraction and purification were the same as those described under (i).

The careful examination of the bases obtained from (i) and (ii) showed that both consisted of *dihydroanhydrotetrahydromethylcryptopine*, since both preparations melted at  $60-63^{\circ}$ , and the mixture also melted at this temperature. The two analyses were made with specimens prepared according to (i) and (ii) respectively:

(i) 0.1126 gave 0.2935  $\text{CO}_2$  and 0.0798  $\text{H}_2\text{O}$ .  $\text{C}=71.1$ ;  $\text{H}=7.9$ .

(ii) 0.1185 „ 0.3077  $\text{CO}_2$  „ 0.0813  $\text{H}_2\text{O}$ .  $\text{C}=70.9$ ;  $\text{H}=7.9$ .

$\text{C}_{22}\text{H}_{29}\text{O}_4\text{N}$  requires  $\text{C}=71.1$ ;  $\text{H}=7.8$  per cent.

This base is characterised by its ready solubility in the usual organic solvents; the salts are readily soluble in water, but sparingly so in dilute acids, and generally crystallise well.

The *hydrochloride*, described above, is almost insoluble in cold dilute hydrochloric acid, and melts at  $213^{\circ}$ . It is very readily

soluble in warm glacial acetic acid, and also in boiling methyl alcohol, and separates from the latter in groups of needles. The addition of potassium iodide to the boiling methyl-alcoholic solution of the hydrochloride gives a clear liquid, from which the hydriodide separates in stars of needles. It is comparatively readily soluble in boiling methyl alcohol, crystallises well, and melts at about  $212^{\circ}$ . The nitrate separates from dilute nitric acid, in which it is very sparingly soluble, as a felted mass of long hairs. The solution of a crystal of the base in a drop of acetic acid gives scarcely any coloration with concentrated sulphuric acid, but the addition of a drop of dilute nitric acid produces an intense brown, changing to deep cherry-red.

*Dihydroanhydrotetrahydromethylcryptopine Methosulphate,*  
 $C_{22}H_{29}O_4N, Me_2SO_4$ .

This well-characterised derivative separates in needles when the solution of the base (2 grams) in benzene (20 c.c.) is mixed with methyl sulphate (2 c.c.). It was collected, washed with benzene, and dried in the steam-oven, when the glistening crystals became opaque and chalky:

0.1210 gave 0.2577  $CO_2$  and 0.0747  $H_2O$ .  $C=58.0$ ;  $H=6.9$ .

$C_{22}H_{29}O_4N, Me_2SO_4$  requires  $C=57.9$ ;  $H=7.0$  per cent.

This methosulphate melts at  $165-167^{\circ}$ , without evolution of gas, to a colourless syrup, and is readily soluble in methyl alcohol or water.

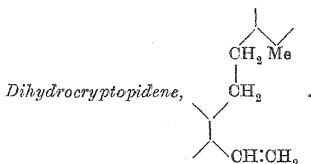
The boiling aqueous solution gives, on the addition of potassium bromide, a milky liquid, from which the methobromide gradually separates in long, well-developed, four-sided, prismatic needles with flat ends.

The *methiodide* is obtained by adding boiling dilute potassium iodide to the boiling dilute aqueous solution of the methosulphate, when the clear solution, on rubbing, deposits tufts of needles:

0.1158 gave 0.2286  $CO_2$  and 0.0657  $H_2O$ .  $C=53.8$ ;  $H=6.2$ .

$C_{22}H_{29}O_4N, MeI$  requires  $C=53.8$ ;  $H=6.2$  per cent.

The dry substance is a satiny mass which darkens at about  $230^{\circ}$  and melts at about  $240^{\circ}$  with very little decomposition.



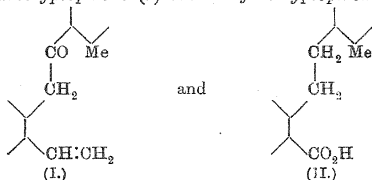
This fine substance is obtained when the methosulphate of dihydroanhydrotetrahydromethylcryptopine is decomposed by methyl-alcoholic potassium hydroxide. The methosulphate (1 gram) dissolves readily in warm methyl-alcoholic potassium hydroxide (10 c.c. of 20 per cent.), and trimethylamine is readily eliminated. After boiling for fifteen minutes, the bulk of the methyl alcohol was distilled off, during which the liquid clouded, and, on adding water, a milky liquid was obtained, which was extracted with much ether. The ethereal solution was thoroughly washed, dried over anhydrous potassium carbonate, and rapidly filtered, when the new substance began to separate immediately as a voluminous mass of soft needles, and a further quantity was obtained from the concentrated ethereal solution. For analysis, the substance was recrystallised from ether:

0.1083 gave 0.2932  $\text{CO}_2$  and 0.0673  $\text{H}_2\text{O}$ .  $\text{C}=73.8$ ;  $\text{H}=6.9$ .

$\text{C}_{20}\text{H}_{22}\text{O}_4$  requires  $\text{C}=73.6$ ;  $\text{H}=6.7$  per cent.

*Dihydrocryptopidene* melts at  $126\text{--}128^\circ$ , or almost at the same temperature as cryptopidene (m. p.  $124^\circ$ ; compare 926), but the mixture of the two substances softens at  $105^\circ$  and is almost completely melted at  $108^\circ$ , so that there can be no question of identity. Moreover, the ethereal solution of dihydrocryptopidene exhibits to only a very slight degree the beautiful lilac fluorescence so characteristic of cryptopidene. Dihydrocryptopidene is unusually sparingly soluble even in boiling methyl alcohol, and separates as a voluminous, woolly mass of needles which fill the entire liquid. The solution of the substance in acetic acid is coloured at first pale brown and then deep cherry-red by sulphuric acid, and a drop of dilute nitric acid changes the colour to intense brown.

*Ketodihydrocryptopidene* (I) and *Dihydrocryptopidenic Acid* (II),



These interesting substances are produced when dihydrocryptopidene is oxidised in acetone solution with permanganate. The substance (2 grams), dissolved in acetone (150 c.c.), was gradually mixed with finely divided permanganate (3 grams) at the ordinary temperature, when, contrary to expectation, oxidation took place rapidly and with the development of so much heat that cooling was necessary in order to keep the temperature below 15°. The product was filtered, the manganese precipitate (A) washed thoroughly with acetone, and the acetone distilled off, when an almost colourless syrup (0.9 gram) remained, which immediately commenced to crystallise, and crystallisation was much hastened by triturating with methyl alcohol. The product was several times recrystallised from methyl alcohol in order to remove traces of unoxidised dihydrocryptopidene:

0.1151 gave 0.2987 CO<sub>2</sub> and 0.0647 H<sub>2</sub>O. C=70.8; H=6.2.

C<sub>20</sub>H<sub>20</sub>O<sub>5</sub> requires C=70.6; H=5.9 per cent.

*Ketodihydrocryptopidene* melts at about 116°, but this melting point is probably not quite accurate, owing to the difficulty of removing the last traces of dihydrocryptopidene. It is characterised by the intense purple coloration which a trace, dissolved in a drop of acetic acid, yields on mixing with much sulphuric acid, and this colour changes to brown on the addition of a drop of dilute nitric acid. When concentrated nitric acid is poured on a trace of the substance rubbed on a watch-glass, a blue solution is produced, and, on warming, a dark green mass separates. *Ketodihydrocryptopidene* does not yield an acetyl derivative when it is boiled with acetic anhydride and anhydrous sodium acetate, since the unchanged substance separates on the addition of water.

*The Semicarbazone*.—This derivative was prepared by boiling the alcoholic solution of crude dihydrocryptopidene (as directly obtained from the oxidation of dihydrocryptopidene) with a large excess of a concentrated aqueous solution of semicarbazide acetate for an hour.

On the addition of water, a caseous mass was precipitated, which was separated into the semicarbazone and dihydrocryptopidine by recrystallisation from methyl alcohol. The semicarbazone is sparingly soluble in methyl alcohol, and crystallises as a voluminous mass of needles melting at about 185—190°:

0.1509 gave 13.2 c.c.  $N_2$  at 12° and 766 mm.  $N=10.2$ .

$C_{21}H_{23}O_5N_3$  requires  $N=10.6$  per cent.

*Dihydrocryptopidenic Acid*.—The manganese precipitate (4, see above) from the oxidation of dihydrocryptopidine was extracted with boiling water, the brown extract boiled with animal charcoal, and acidified, when a viscid acid separated, which gradually hardened and immediately became crystalline on rubbing with glacial acetic acid. This was collected, drained on porous porcelain, and dissolved in boiling glacial acetic acid, from which the new acid separated in long, prismatic needles.

The recrystallised acid yielded the following analytical results:

0.1045 gave 0.2522  $CO_2$  and 0.0572  $H_2O$ .  $C=65.8$ ;  $H=6.1$ .

0.1142 „ 0.2777  $CO_2$  „ 0.0627  $H_2O$ .  $C=66.2$ ;  $H=6.1$ .

$C_{19}H_{20}O_6$  requires  $C=66.3$ ;  $H=5.8$  per cent.

*Dihydrocryptopidenic acid* melts at 194—195°, and is sparingly soluble in cold methyl alcohol, but dissolves more readily on boiling, and crystallises in stars of slender needles; it is almost insoluble in cold water. The solution in glacial acetic acid gives, with sulphuric acid, an olive-brown coloration, which becomes redder on the addition of a drop of dilute nitric acid. When concentrated sulphuric acid is poured on a trace of the acid rubbed on a watch-glass, an intense green colour is produced, which soon changes to purplish-brown, and a green precipitate separates on the addition of water. Concentrated nitric acid does not give a colour reaction with the acid.

The sodium and potassium salts of the acid are readily soluble and give with hydrochloric acid a gelatinous precipitate, which only very gradually becomes crystalline. The titration with  $N/10$ -sodium hydroxide did not give very accurate results, owing to the uncertainty of the end-point. In one experiment, 0.308 neutralised 0.0385  $NaOH$ , whereas this amount of a monobasic acid,  $C_{19}H_{20}O_6$ , should neutralise 0.0359  $NaOH$ .

*The Anilide*,  $C_{18}H_{19}O_4 \cdot CO \cdot NH \cdot C_6H_5$ .—This derivative was prepared mainly with the object of controlling the composition of the acid. The acid was warmed with excess of freshly distilled phosphorus trichloride at 60—70°, when it dissolved completely and with very little discoloration. The excess of the trichloride was then distilled off under reduced pressure and the residue mixed

with much dry ether and excess of aniline. The ethereal solution was washed with very dilute hydrochloric acid, then with water, and the ether evaporated, when a crystalline residue was obtained which was digested with dilute ammonia in order to remove any traces of unchanged acid. Finally, the anilide was recrystallised from glacial acetic acid, from which it separated in glistening needles melting at about  $185^{\circ}$ :

0.1128 gave 0.2953  $\text{CO}_2$  and 0.0597  $\text{H}_2\text{O}$ .  $\text{C}=71.4$ ;  $\text{H}=5.9$ .

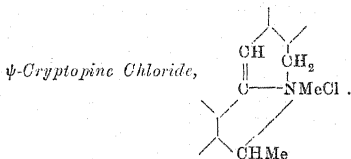
$\text{C}_{25}\text{H}_{25}\text{O}_5\text{N}$  requires  $\text{C}=71.6$ ;  $\text{H}=6.0$  per cent.

#### Section IV.

##### *The Quaternary Salts of $\psi$ -Cryptopine.*

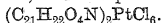
During the course of this investigation, it has been necessary on several occasions to make a close comparison of certain quaternary salts, thought to be new, with the corresponding quaternary salts of  $\psi$ -cryptopine, and this has necessitated a more accurate characterisation of the latter than had been made in Part I. of this research (984).

The following is a brief account of the principal properties of these interesting salts.



The formation of this salt from anhydrocryptopine methosulphate by boiling with concentrated hydrochloric acid has already been described (984), but the method of preparation there recommended may be simplified in the following manner. Anhydrocryptopine methosulphate (10 grams) is mixed in a small flask with concentrated hydrochloric acid (20 c.c.), gently warmed until solution is complete, and the whole boiled for five minutes in such a way that about a third of the hydrochloric acid escapes; the pale brown syrup is then mixed with two volumes of boiling water. On remaining in the ice-chest, the liquid becomes filled with needles of  $\psi$ -cryptopine chloride, which is collected, washed with dilute hydrochloric acid, and recrystallised from this solvent. The yield is about 60 per cent. of that theoretically possible, and a further small quantity may be obtained by allowing the brown mother

liquor to concentrate over solid potassium hydroxide in a vacuum desiccator. The remaining mother liquor contains a considerable quantity of quaternary salt, the nature of which has not been established. When  $\psi$ -cryptopine chloride is dried at  $100^{\circ}$  until it has lost its water of crystallisation, the residue is much discoloured and sometimes brick-red; there was therefore a possibility that the original analysis of the anhydrous chloride was untrustworthy. Further analyses leave, however, no doubt that the chloride has the formula  $C_{21}H_{22}O_4NCl$  originally assigned to it, and this is confirmed by the analyses of the iodide,  $C_{21}H_{22}O_4NI$ , the bromide,  $C_{21}H_{22}O_4NBr$ , and the platinichloride,



In order to determine the actual composition of the crystallised chloride, two specimens were repeatedly crystallised from dilute hydrochloric acid and left on watch-glasses in the dark until the weight was constant. The substance melted at  $117$ – $120^{\circ}$  with evolution of steam, solidified again, and then melted at about  $150$ – $152^{\circ}$ , with evolution of gas, to an orange-red froth. The determination of the water of crystallisation was made by drying in the steam-oven in the case of (a) and (b), and the analysis (c) was done with substance which had been dried over phosphoric oxide in a vacuum desiccator, when the whole of the water was thereby removed with scarcely any discoloration:

(a) 0.1389 lost 0.0290.  $H_2O = 20.9$ .

(b) 0.8106 „ 0.1628.  $H_2O = 21.1$ .

(c) 0.1099 gave 0.2611  $CO_2$  and 0.0593  $H_2O$ .  $C = 64.6$ ;  $H = 6.0$ .

$C_{21}H_{22}O_4NCl \cdot 6H_2O$  contains  $H_2O = 21.7$  per cent.

$C_{21}H_{22}O_4NCl$  requires  $C = 65.0$ ;  $H = 5.7$  per cent.

Dry  $\psi$ -cryptopine chloride crystallises from anhydrous methyl alcohol, in which it is readily soluble, in clusters of needles which, when heated at  $100^{\circ}$ , become opaque, and the anhydrous residue darkens at  $190^{\circ}$ , is very dark at  $205^{\circ}$ , and melts at  $210^{\circ}$  with effervescence to a black froth:

0.1048 gave 0.2498  $CO_2$  and 0.0556  $H_2O$ .  $C = 65.0$ ;  $H = 5.9$ .

$C_{21}H_{22}O_4NCl$  requires  $C = 65.0$ ;  $H = 5.7$  per cent.

In addition to the remarkable colour changes already recorded (985), it may be mentioned that the solution of  $\psi$ -cryptopine chloride in dilute sulphuric acid gives a reddish-violet on dusting in finely divided manganese dioxide, and an intense cherry-red develops on boiling.

A series of experiments on the action of dilute hydrochloric acid on anhydrocryptopine methosulphate was made with the object of determining whether this substance would behave towards dilute

acids in a manner similar to that which leads, under these conditions, to the formation of the hydroxyisoanhydrodihydrocryptopines from anhydrocryptopine itself (994).

The unexpected result was, however, obtained that, even when boiled with dilute hydrochloric acid, anhydrocryptopine methosulphate loses an *N*-methyl group and yields  $\psi$ -cryptopine chloride. Thus the methosulphate (2 grams), heated on the steam-bath for forty minutes with concentrated hydrochloric acid (2 c.c.) and water (5 c.c.), gives a deep yellow solution. On keeping in the ice-chest, this deposits a mass of needles which, on examination and analysis, proved to be  $\psi$ -cryptopine chloride.

*$\psi$ -Cryptopine Bromide*,  $C_{21}H_{22}O_4NBr$ .—In preparing this characteristic salt, carefully purified  $\psi$ -cryptopine chloride, dissolved in boiling water, was mixed with a large excess of boiling potassium bromide, when a clear solution resulted, from which microscopic needles soon separated. The bromide was collected, recrystallised from dilute potassium bromide, and then once from water. The air-dry salt contains apparently  $5H_2O$ , all of which is lost at  $95^\circ$ :

0.1165, heated at  $95^\circ$ , lost 0.0204.  $H_2O = 17.6$ .

0.1165 gave 0.2476  $CO_2$  and 0.0533  $H_2O$ .  $C = 58.0$ ;  $H = 5.1$ .

$C_{21}H_{22}O_4NBr \cdot 5H_2O$  contains  $H_2O = 17.2$ , and  $C_{21}H_{22}O_4NBr$  requires  $C = 58.3$  and  $H = 5.1$  per cent.

This bromide exists in well-defined, dimorphic forms. The needles (*A*) from water, dried at  $90^\circ$ , melt with decomposition at about  $130$ – $135^\circ$ ; solidification then takes place, and the next melting point observed is about  $230^\circ$  with effervescence to a reddish-brown froth. When the anhydrous substance (*A*) is boiled with ethyl or methyl alcohol, it dissolves, and the solution now deposits well-developed prisms (*B*), which become opaque in the steam-oven.

The modification (*B*) melts at about  $245^\circ$  with vigorous effervescence to a reddish-brown froth, and crystallises particularly well from glacial acetic acid as a mass of glistening, sulphur-yellow prisms, which Mr. T. V. Barker has described as follows. The macroscopic crystals are strongly doubly refracting, stout, rectangular prisms with straight extinction. In convergent light, an optic axis nearly central. When crystallisation is rapid, there is a marked tendency to form lenticular crystals having diagonal extinction. The modification (*A*) becomes slate-coloured on exposure to light, and is comparatively readily soluble in boiling water, yielding a nearly colourless solution which gelatinises on rapid cooling. Modification (*B*) is sparingly soluble in hot water, and becomes deep salmon on exposure to light. Both modifications



give the remarkable colour reactions which have been described in detail in the case of the corresponding chloride (985).

*ψ-Cryptopine Iodide*,  $C_{21}H_{22}O_4NI$ .—This substance has been described (984) as a glistening mass of scales melting at 232—235°.

During the preparation of larger quantities, it was observed that this iodide exists in dimorphic modifications (*A*) and (*B*), melting at 225—227° and 240—242° respectively. When a hot solution of *ψ*-cryptopine chloride is mixed with hot dilute potassium iodide, a heavy, crystalline precipitate separates, which becomes brick-red at 220°, melts at 232—235°, and consists of modification (*A*). It may be recrystallised from methyl alcohol, if the operation is rapidly carried out, and is obtained in flat, prismatic needles. When, however, it is boiled for a considerable time with methyl alcohol insufficient completely to dissolve it, the needles gradually give place to short, well-defined prisms which are exceedingly sparingly soluble even in boiling methyl alcohol, melt at 240—242°, and consist of modification (*B*). This modification is also sparingly soluble in boiling glacial acetic acid, and separates in iridescent, yellow scales resembling lead iodide, and these, under the microscope, are seen to consist of flat prisms with truncated ends.

*ψ-Cryptopine Hydrogen Sulphate*,  $C_{21}H_{22}O_4N,HSO_4$ .—This quaternary salt is obtained when anhydrocryptopine methosulphate (5 grams), dissolved in water (13 c.c.) and sulphuric acid (2 c.c.), is heated for two hours on the steam-bath. On remaining in the ice-chest, the deep yellow solution deposits a crystalline mass which, under the microscope, is seen to consist of warts and to be quite homogeneous.

This was collected, recrystallised from dilute sulphuric acid, in which it is rather sparingly soluble, washed twice with a little water, and drained on porous porcelain. It was then recrystallised from a little water and dried in the steam-oven:

0.1116 gave 0.2315  $CO_2$  and 0.0530  $H_2O$ .  $C=56.5$ ;  $H=5.3$ .

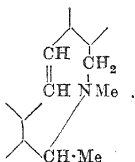
$C_{21}H_{22}O_4N,HSO_4$  requires  $C=56.1$ ;  $H=5.1$  per cent.

*ψ-Cryptopine hydrogen sulphate* becomes yellow at 180°, deep yellow at 200°, and decomposes at about 215—220° to an orange-red froth.

It exhibits in a very striking manner the characteristic colour reactions described in detail in the case of *ψ*-cryptopine chloride (985). The relationship of the sulphate to the latter is also evidenced by the fact that, on precipitation with potassium iodide, both yield the (*A*) and (*B*) modifications of *ψ*-cryptopine iodide (see above). A rather concentrated solution of the sulphate gives, on the addition of dilute nitric acid, an immediate chalky

precipitate of the nitrate; this dissolves on warming and separates in a highly characteristic manner, namely, as an iridescent mass which, under the microscope, is seen to consist of thin, lenticular or boat-shaped plates.

*Section IV (a). The Reduction of  $\psi$ -Cryptopine Chloride in Alkaline Solution: Formation of  $\psi$ -Anhydrodihydrocryptopine (A) (841),*



When  $\psi$ -cryptopine chloride (2 grams),\* dissolved in water (100 c.c.) and rendered slightly alkaline by the addition of sodium hydroxide, is placed on crushed sodium amalgam (50 grams of 4 per cent.) and the whole heated on the steam-bath, a viscid base soon commences to separate, which gradually crystallises and ultimately becomes quite hard. When the separation was complete, the base was collected, thoroughly washed, dissolved in methyl alcohol, mixed with much ether, and the solution washed until free from methyl alcohol, during which a small quantity of a slimy, quaternary salt separated, which was not examined. After filtering and drying over potassium carbonate, the claret-coloured solution was concentrated considerably and left in the ice-chest, when a thick crust of pale brown prisms gradually separated, which were collected and washed with ether. The mother liquor was evaporated, and the residual purplish-brown syrup mixed with methyl alcohol and nucleated with a crystal from the first crop, when it immediately began to crystallise, and, after collecting and washing with a little methyl alcohol, a considerable pale brown, crystalline mass remained. The combined crops were recrystallised from methyl alcohol, from which the new substance separates splendidly in short, glistening needles growing to stout prisms:

0.1240 gave 0.3255  $\text{CO}_2$  and 0.0728  $\text{H}_2\text{O}$ .  $\text{C}=71.5$ ;  $\text{H}=6.5$ .

$\text{C}_{21}\text{H}_{23}\text{O}_4\text{N}$  requires  $\text{C}=71.4$ ;  $\text{H}=6.5$  per cent.

\* Not more than 2 grams should be employed and the experiment should be conducted as rapidly as possible, otherwise the product will be very dark coloured owing to the formation of a black base due to the action of the alkali on  $\psi$ -cryptopine chloride (985).

The prisms have been measured by Mr. T. V. Barker.

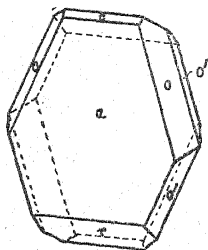
The platy crystals of this substance belong to the monoclinic system. Crystallographic constants:  $21^{\circ}3'$ ,  $a(73^{\circ}13')m(16^{\circ}47')b$ ,  $43^{\circ}13'$ ,  $74^{\circ}18'$ , or, alternatively,  $a : b : c = 3.446 : 1 : 2.598$ ,  $\beta = 105^{\circ}42'$ . The habit of the crystals is shown in Fig. 3, the observed forms being  $a(100)$ ,  $c(001)$ ,  $r(\bar{1}01)$ ,  $o'(\bar{1}11)$ , and  $o(111)$ . Two crystals were measured on the two-circle goniometer, with the following results:

	$a(100)$ .	$c(001)$ .	$r(\bar{1}01)$ .	$o'(\bar{1}11)$ .	$o(111)$ .
Azimuth	Face of	$90^{\circ} 0'$	$90^{\circ} 0'$	$21^{\circ} 3'$	$21^{\circ}17' (21^{\circ}3')$
Polar distance reference	$74^{\circ} 18'$	$116^{\circ} 40'$	$100^{\circ} 18' (100^{\circ}14')$	$69^{\circ} 29' (69^{\circ} 4')$	

Determinants:  $121/121/10\bar{1}$ . Complex-symbol:  $3d$ ;  $-1/69\frac{1}{2}/-9\frac{1}{2}$ .

Optically, the extinction on  $a(100)$  is parallel with the edge  $ac$ . In convergent light, a wide biaxial figure is visible through  $a$ , indicating the symmetry plane as plane of the optic axes.

FIG. 3.



$\psi$ -Anhydrodihydrocryptopine (*A*) melts at  $112^{\circ}$ , and is very readily soluble in benzene, ether, or acetone, but sparingly so in light petroleum.

The solution of a trace in a drop of acetic acid gives, with sulphuric acid, a deep orange-red coloration, and the addition of a drop of dilute nitric acid changes this to crimson, which becomes more intense on warming. A trace rubbed on a watch-glass is coloured deep brown by concentrated nitric acid. The hydrochloride and sulphate of the base are readily soluble and exhibit little tendency to crystallise, but the nitrate is characteristic. This salt is obtained, when the base is rubbed with dilute nitric acid, as a crystalline mass very sparingly soluble in cold dilute nitric acid; it dissolves, however, on warming and separates in stars of long, thin plates. The sparing solubility and tendency to crystallise of

this salt have been made use of, with success, in purifying dark-coloured specimens of the crude base. The solution of the sulphate gives, on the addition of potassium iodide, a milky liquid, from which the iodide separates on rubbing, and crystallises from water, in which it is rather readily soluble, in six-sided prisms.

*The Methosulphate*,  $C_{21}H_{23}O_4N, Me_2SO_4$ .—The solution of  $\psi$ -anhydrodihydrocryptopine (A) (2 grams) in warm benzene reacts readily with methyl sulphate (2 c.c.) with considerable rise of temperature, and, if a crystal of the methosulphate is introduced and the whole allowed to remain in the ice-chest, a hard crust of nodules separates. If a crystal is not available, the methosulphate generally separates as a syrup, which, however, after washing with ether and stirring with ether, rapidly crystallises. For analysis, the substance was recrystallised from water, in which it is readily soluble; it separates in groups of short, prismatic needles:

0.1177 gave 0.2460  $CO_2$  and 0.0646  $H_2O$ .  $C=57.1$ ;  $H=6.1$ .

$C_{21}H_{23}O_4N, Me_2SO_4$  requires  $C=57.6$ ;  $H=6.1$  per cent.

*$\psi$ -Anhydrodihydrocryptopine (A) methosulphate* melts at  $175-180^\circ$  with some effervescence, but without darkening; the solution of a trace in acetic acid gives with sulphuric acid a deep burnt sienna coloration, becoming intense permanganate on the addition of a drop of dilute nitric acid. It is readily soluble in hot methyl alcohol, and when boiled with methyl-alcoholic potassium hydroxide, the solution becomes deep violet, especially where it comes in contact with the air; the colour then changes to bluish-violet, then to sage-green; the addition of hydrochloric acid destroys the green colour and yields a clear, burnt sienna solution.

*The Methiodide*,  $C_{21}H_{23}O_4N, MeI$ .—The addition of hot dilute potassium iodide to the hot dilute solution of the methosulphate results in a clear solution, from which the methiodide immediately begins to separate in well-developed, six-sided prisms with bevelled edges:

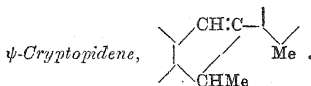
0.1172 gave 0.2315  $CO_2$  and 0.0602  $H_2O$ .  $C=53.9$ ;  $H=5.7$ .

$C_{21}H_{23}O_4N, MeI$  requires  $C=53.3$ ;  $H=5.3$  per cent.

*$\psi$ -Anhydrodihydrocryptopine methiodide* is sparingly soluble in boiling methyl alcohol, and separates in long, prismatic needles radiating from a centre. It melts at  $197-200^\circ$ , with vigorous effervescence to a yellow froth.

*Oxidation of  $\psi$ -Anhydrodihydrocryptopine (A)*.—When this base (2 grams) was treated in acetone solution with powdered permanganate (2.5 grams), it was noticed that oxidation was slow, and, on working up the product, about half the substance was

recovered unchanged. The aqueous extract from the manganese precipitate yielded, on concentrating and acidifying, a small quantity of a highly coloured acid resembling amorphous phosphorus, and this did not appear to contain any 5:6-methylene-dioxy-*o*-toluic acid (compare p. 728).



This characteristic substance is produced directly from *ψ*-anhydrodihydrocryptopine (4) methosulphate by reduction with sodium amalgam in faintly alkaline solution. The methosulphate (8 grams), dissolved in hot water (200 c.c.), was poured on crushed sodium amalgam (150 grams of 3 per cent.) in a flat basin, when, on heating on the steam-bath, there was an immediate odour of dimethylamine, and a crystalline scum began to rise to the surface. After about half an hour, there was no further separation; the whole was therefore filtered, and the colourless, crystalline residue washed and recrystallised from methyl alcohol. The yield appeared to be almost that theoretically possible:

0.1121 gave 0.3052 CO<sub>2</sub> and 0.0628 H<sub>2</sub>O. C=74.2; H=6.2.

C<sub>20</sub>H<sub>20</sub>O<sub>4</sub> requires C=74.1; H=6.2 per cent.

*ψ*-Cryptopidene melts at 142—144°, and cannot be identical with *iso-ψ*-cryptopidene (m. p. 152°, p. 776), since the mixture of the two substances melts at about 130—132° with previous softening. It is sparingly soluble in cold methyl alcohol, but dissolves more readily on boiling, and separates in groups of nearly colourless, glistening needles. It dissolves readily in boiling alcohol, benzene, acetone, or acetic acid, but is sparingly soluble in ether or light petroleum. It crystallises well from light petroleum in six-sided plates, and from acetone or dilute acetic acid in needles. The solution of a trace in acetic acid gives, with sulphuric acid, a burnt sienna coloration which, on the addition of a drop of dilute nitric acid, becomes deep brown. Concentrated nitric acid dissolves the substance to a deep brown solution, which gradually fades. A crystal of the substance dissolved in acetic acid gives, with manganese dioxide and dilute sulphuric acid, an intense brown solution.

*ψ*-Cryptopidene does not appear to be reduced when its solution in boiling alcohol is treated with sodium (compare p. 745).

*Oxidation of ψ-Cryptopidene.*—In this experiment, the substance (3.5 grams), dissolved in acetone (200 c.c.), was oxidised by the gradual addition of finely powdered permanganate (5 grams) at

the ordinary temperature. The product was filtered, and the manganese precipitate, after thoroughly washing with acetone, extracted with boiling water. The brown, alkaline extract was nearly neutralised, boiled with animal charcoal, concentrated, and acidified, when an acid (0.5 gram) separated which crystallised from acetic acid in needles, melted at  $214-216^{\circ}$ , and was recognised as 5:6-methylenedioxy-*o*-toluic acid (916). The acetone extract from the oxidation yielded, on evaporation, a syrupy mass (2.9 grams), which, when rubbed with methyl alcohol, immediately crystallised. After filtering and leaving in contact with porous porcelain, the yellow mass was once crystallised from methyl alcohol, when it separated in pale yellow needles melting at about  $128^{\circ}$ . On careful fractional crystallisation from methyl alcohol, three distinct kinds of crystals were observed; these were mechanically separated, and each kind was recrystallised. The three constituents were found to be (i) unchanged  $\psi$ -cryptopidine melting at  $140-142^{\circ}$ ; *dioxy- $\psi$ -cryptopidine*,  $C_{20}H_{18}O_6$ , melting at  $138-140^{\circ}$  and crystallising in light, woolly balls; *trioxy- $\psi$ -cryptopidine*,  $C_{20}H_{18}O_7$ , melting at  $165^{\circ}$  and crystallising in hard, single, sulphur-yellow prismatic needles.

The analysis of *dioxy- $\psi$ -cryptopidine* yielded the following results:

0.1071 gave 0.2640  $CO_2$  and 0.0481  $H_2O$ . C=67.2; H=5.2.

$C_{20}H_{18}O_6$  requires C=67.8; H=5.1 per cent.

The solution of a trace of this substance in acetic acid gives with sulphuric acid an intense brown coloration, becoming purplish-brown and then cherry-red on the addition of a drop of dilute nitric acid. It reacts readily when its solution in methyl alcohol is boiled with excess of semicarbazide hydrochloride and sodium acetate, and a crystalline precipitate of the *semicarbazone* separates which is very sparingly soluble in methyl alcohol.

Found: N=11.3.

$C_{21}H_{21}O_6N_3$  requires N=10.2 per cent.

The behaviour of *dioxy- $\psi$ -cryptopidine* towards alkalis resembles that of benzoin or benzil. Methyl-alcoholic potassium hydroxide does not immediately colour the substance, but gradually a reddish-brown develops, and, on warming, this becomes intense reddish-brown, then pink, and then gradually fades.

The product, diluted with water, yields a pale brown solution, and hydrochloric acid precipitates an amorphous acid which, on warming, becomes crystalline.

*Trioxy- $\psi$ -cryptopidine* (m. p.  $165^{\circ}$ ) yielded the following analytical results:

0.1070 gave 0.2539  $\text{CO}_2$  and 0.0478  $\text{H}_2\text{O}$ .  $\text{C}=64.7$ ;  $\text{H}=5.0$ .

$\text{C}_{20}\text{H}_{18}\text{O}_7$  requires  $\text{C}=64.9$ ;  $\text{H}=4.9$  per cent.

The acetic acid solution of a trace of this substance is coloured yellowish-brown by sulphuric acid, and the addition of a drop of dilute nitric acid changes this first to port-wine colour and then to intense burnt sienna. It also reacts very readily when its solution in boiling methyl alcohol is mixed with excess of a saturated aqueous solution of semicarbazide hydrochloride and sodium acetate, and a voluminous, rather gelatinous precipitate separates which appears to be the *disemicarbazone* mixed probably with some of the mono-derivative.

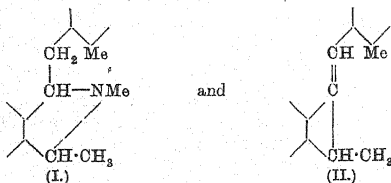
Found:  $\text{N}=15.7$ .

$\text{C}_{21}\text{H}_{21}\text{O}_7\text{N}_3$  requires  $\text{N}=9.8$ ;  $\text{C}_{22}\text{H}_{24}\text{O}_7\text{N}_6$  requires  $\text{N}=17.3$  per cent.

Trioxo- $\psi$ -cryptopidene, like the corresponding dioxy-derivative (see above), exhibits the benzil reaction in a striking manner. The powdered substance is rapidly coloured brown when mixed with methyl-alcoholic potassium hydroxide, and dissolves to an intense reddish-brown solution, which becomes pink in contact with air, and then soon fades, but not completely. The solution of the product in water is pale salmon, and yields a brick-red, crystalline precipitate on the addition of dilute hydrochloric acid.

Constitutional formulæ which appear to be in harmony with the properties of dioxy- and trioxo- $\psi$ -cryptopidene are suggested on p. 729.

*Section IV (b). The Reduction of  $\psi$ -Cryptopine Chloride in Acid Solution: Formation of Dihydroanhydro- $\psi$ -cryptopine (I) and iso- $\psi$ -Cryptopidene (II),*



In studying this curious reduction,  $\psi$ -cryptopine chloride (5 grams), dissolved in water (80 c.c.) and concentrated hydrochloric acid (15 c.c.), was treated at the boiling temperature, in an enamelled iron basin, with sodium amalgam (200 grams of 4 per cent.), which was added all at once. The whole was well

stirred during the reduction, and care was taken, by frequently adding small quantities of hydrochloric acid, that the liquid was always strongly acid. During the process, a white, crystalline, insoluble substance (iso- $\psi$ -cryptopidine) separated in quantity equal to about 8 per cent. of the  $\psi$ -cryptopine chloride employed; this was collected, and its examination is described on p. 776.

The acid filtrate from this neutral substance was mixed with excess of ammonia, when a caseous precipitate separated which, on shaking, became chalky, and this was collected, washed, and drained on porous porcelain. The nearly colourless mass was dissolved in methyl alcohol and poured into a large volume of ether, when a flocculent precipitate of unchanged  $\psi$ -cryptopine chloride separated, which was collected and well washed with ether. The pale brown ethereal filtrate was washed with water until free from methyl alcohol, dried over potassium carbonate, and concentrated to a small bulk, but nothing separated after remaining in the ice-chest for a week. When the ether was evaporated, a syrup remained which, over phosphoric oxide in a vacuum desiccator, became a friable mass like colophony, and consisted of almost pure *dihydroanhydro- $\psi$ -cryptopine*:

0.1265 gave 0.3271  $\text{CO}_2$  and 0.0806  $\text{H}_2\text{O}$ .  $\text{C}=70.5$ ;  $\text{H}=7.0$ .

$\text{C}_{21}\text{H}_{25}\text{O}_4\text{N}$  requires  $\text{C}=71.0$ ;  $\text{H}=7.0$  per cent.

All attempts to obtain this base in a crystalline condition were unsuccessful, and it is fortunate that it yields a characteristic *picrate* which separates as a deep ochreous, amorphous precipitate when picric acid is added to the aqueous solution of the hydrochloride. This double salt melts under boiling water, and is sparingly soluble in boiling methyl alcohol, from which it separates in deep orange leaflets. After drying in the steam-oven, the substance becomes yellow at  $110^\circ$ , shrinks at  $180^\circ$ , and melts at about  $195$ — $197^\circ$  to a reddish-brown syrup:

0.1021 gave 8.7 c.c.  $\text{N}_2$  at  $13^\circ$  and 755 mm.  $\text{N}=10.0$ .

$\text{C}_{21}\text{H}_{25}\text{O}_4\text{N} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$  requires  $\text{N}=9.6$  per cent.

This *picrate* was decomposed by ammonia, the base extracted with ether, the ethereal solution washed, dried over potassium carbonate, evaporated, and the syrup left over phosphoric oxide in a vacuum desiccator until it became a friable resin and the weight was constant. The analysis then yielded  $\text{C}=70.9$ ;  $\text{H}=7.0$ , agreeing well with the formula  $\text{C}_{21}\text{H}_{25}\text{O}_4\text{N}$ , which requires  $\text{C}=71.0$ ;  $\text{H}=7.0$  per cent.

*Oxidation of Dihydroanhydro- $\psi$ -cryptopine*.—When the solution of the base (1 gram) in acetone is treated with finely divided permanganate (1.2 grams), oxidation takes place moderately readily at  $15^\circ$ .



The manganese precipitate, after thoroughly washing with acetone, yielded on extraction with hot water a deep brown solution, from which hydrochloric acid precipitated a dark, resinous acid. This was collected, boiled with much water, the extract decolorised with animal charcoal, neutralised with sodium carbonate, and evaporated to a small bulk.

On acidifying the nearly colourless solution, a chalky acid separated, which crystallised from acetic acid as a colourless, satiny mass, melted at  $214-216^{\circ}$ , and was recognised as 5:6-methylenedioxy-*o*-toluic acid,  $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_2\text{Me}\cdot\text{CO}_2\text{H}$  (916). The acetone solution from the oxidation deposited a syrup on evaporation which was only partly soluble in warm dilute hydrochloric acid, but the amount was too small for further investigation.

*iso-ψ-Cryptopidene*,  $\text{C}_{20}\text{H}_{20}\text{O}_4$ .—The neutral substance formed during the reduction of *ψ*-cryptopine chloride (see above) was well washed, dried on porous porcelain, and twice recrystallised from methyl alcohol:

0.1047 gave 0.2838  $\text{CO}_2$  and 0.0598  $\text{H}_2\text{O}$ .  $\text{C}=73.9$ ;  $\text{H}=6.3$ .

0.1023 „ 0.2768  $\text{CO}_2$  „ 0.0553  $\text{H}_2\text{O}$ .  $\text{C}=73.8$ ;  $\text{H}=6.0$ .

$\text{C}_{20}\text{H}_{20}\text{O}_4$  requires  $\text{C}=74.1$ ;  $\text{H}=6.0$  per cent.

*iso-ψ-Cryptopidene* melts at  $150-152^{\circ}$ , and is moderately soluble in boiling methyl alcohol, from which it crystallises in glistening plates resembling benzoic acid. It dissolves readily in benzene, but is almost insoluble in light petroleum, and separates, when the hot solution in benzene is mixed with light petroleum, in thin, rhombic plates.

It also crystallises well from acetone in almost square plates with bevelled edges. It is readily soluble in boiling glacial acetic acid, much less so in the cold, and separates splendidly as a satiny mass of thin, rectangular plates. The solution of a crystal in a drop of acetic acid gives, on the addition of sulphuric acid, a deep brown coloration, which becomes much more intense on adding a drop of dilute nitric acid.

A trace of the substance rubbed on a watch-glass dissolves in concentrated nitric acid, and the intense indigo-blue coloration produced soon changes to brown. The most characteristic reaction of the substance is the intense pink colour, changing to brown, which develops when finely powdered manganese dioxide and a little dilute sulphuric acid is added to the solution in dilute acetic acid. *iso-ψ-Cryptopidene* does not appear to be readily reduced when its solution in boiling alcohol is treated with sodium.

*Oxidation of iso-ψ-Cryptopidene to Ketodihydroiso-ψ-cryptopidene*.—*iso-ψ-Cryptopidene* is scarcely attacked when its solution in acetone is mixed with permanganate at  $-10^{\circ}$ , and action is

very slow even at the ordinary temperature. In order to study this oxidation, the substance (1.4 grams), dissolved in acetone (50 c.c.), was, during two days, gradually mixed with very finely powdered and sieved permanganate (2 grams).

The product was filtered, the manganese precipitate thoroughly washed with acetone (*B*), and extracted with boiling water. The brown, aqueous solution was decolorised with animal charcoal, concentrated, and acidified, when a small quantity of a solid acid separated which crystallised from acetic acid in satiny plates, melted at 215—217°, and consisted of 5:6-methylenedioxy-*o*-toluic acid (916).

The acetone solution (*B*) deposited, on evaporation, a yellow syrup, and this yielded, when distilled in a current of steam, a small quantity of 5:6-methylenedioxy-*o*-tolualdehyde (907), which separated from the distillate in needles and melted at 72—74°. The residue in the steam distillation flask was extracted with ether, the ethereal solution thoroughly dried over potassium carbonate, and evaporated, when a syrup remained, which soon crystallised. After remaining in contact with porous porcelain until oily impurity had been removed, the almost colourless residue was fractionally crystallised from methyl alcohol, and thus separated into unchanged *iso*- $\psi$ -cryptopidene and a new substance, which crystallised in glistening plates, melted at about 135°, and consisted of *ketodihydroiso*- $\psi$ -*cryptopidene*. Unfortunately, the small amount of material available did not allow of the removal of the last traces of *iso*- $\psi$ -cryptopidene, so that the melting point must be taken as approximate only:

0.1102 gave 0.2861 CO<sub>2</sub> and 0.0589 H<sub>2</sub>O. C=70.8; H=5.9.

C<sub>20</sub>H<sub>20</sub>O<sub>5</sub> requires C=70.6; H=5.9 per cent.

The small remainder of the substance was dissolved in boiling methyl alcohol, digested with excess of semicarbazide hydrochloride and sodium acetate for two hours, and evaporated to dryness. The nearly white residue was washed with water and crystallised from alcohol, from which it separated in needles:

0.1001 gave 0.2348 CO<sub>2</sub> and 0.0522 H<sub>2</sub>O. C=64.0; H=5.9.

C<sub>21</sub>H<sub>23</sub>O<sub>5</sub>N<sub>3</sub> requires C=63.5; H=5.8 per cent.

Attempts to hydrolyse this *semicarbazone* with a view to obtaining the pure keto-derivative were unsuccessful, since boiling with concentrated hydrochloric acid converts it into a substance which crystallises from methyl alcohol in needles, melts at about 225°, and is possibly an indole derivative. A constitutional formula for *ketodihydroiso*- $\psi$ -*cryptopidene* is suggested on p. 730.

*Section IV (c). The Reduction of  $\psi$ -Methylberberinium Chloride :  
Formation of iso- $\psi$ -Berberidene and Dihydroanhydro- $\psi$ -methyl-  
berberine.*

This reduction was carried out essentially under the conditions described in detail in the case of the acid reduction of  $\psi$ -cryptopine chloride (p. 774), 300 grams of 4 per cent. amalgam being employed for the reduction of 8 grams of the chloride. During the process, a scum separated, which at first was crystalline, but later melted to a brown syrup, and, after the product had cooled, this was extracted with ether (A), the ethereal solution well washed, dried over potassium carbonate, and evaporated, when a syrup remained which showed no signs of crystallising. However, on rubbing with methyl alcohol, crystallisation soon commenced, and, after collecting and washing with methyl alcohol, the pale salmon mass was twice recrystallised from this solvent:

0.1187 gave 0.3207  $\text{CO}_2$  and 0.0677  $\text{H}_2\text{O}$ .  $\text{C}=73.7$ ;  $\text{H}=6.3$ .

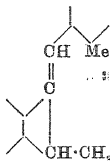
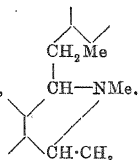
0.1195 „ 0.3245  $\text{CO}_2$  „ 0.0687  $\text{H}_2\text{O}$ .  $\text{C}=74.1$ ;  $\text{H}=6.4$ .

$\text{C}_{20}\text{H}_{20}\text{O}_4$  requires  $\text{C}=74.1$ ;  $\text{H}=6.2$  per cent.

iso- $\psi$ -Berberidene melts at  $117^\circ$  and is sparingly soluble in methyl alcohol, yielding a lilac, fluorescent solution, from which it separates in well-developed prismatic needles. It is very readily soluble in benzene, but less so in light petroleum, and separates from the mixture of these solvents particularly well in brilliant, elongated prisms. It also crystallises well from light petroleum alone or from ether, in which it is readily soluble, or from acetic acid, in glistening prisms.

A trace of the substance rubbed on the side of a test-tube is coloured deep violet, changing to brown by concentrated nitric acid.

The solution in acetic acid is coloured yellowish-brown on the addition of sulphuric acid, and a drop of dilute nitric acid changes the colour to an intense reddish-brown. When manganese dioxide and a little dilute sulphuric acid are added to the solution in acetic acid in the cold, a pink colour gradually develops, and, on warming, this changes to brown and then to yellow. The relationship of iso- $\psi$ -berberidene and iso- $\psi$ -cryptopidine is discussed on p. 731, and it may be pointed out that the striking similarity in their properties is doubtless due to their both containing the characteristic grouping

*Dihydroanhydro-ψ-methylberberine,*

The acid liquors (A) from the reduction of  $\psi$ -methylberberinium chloride, which had been extracted with ether, as already described, were made strongly alkaline with ammonia, and the turbid liquid thoroughly extracted with ether. On evaporation, the ethereal solution deposited a syrup, which was only partly soluble in dilute hydrochloric acid.

The whole was warmed with very dilute hydrochloric acid, filtered, and the filtrate precipitated with excess of picric acid, when a voluminous, viscid mass separated, which soon hardened. This was collected, left on porous porcelain until dry, and recrystallised from methyl alcohol, from which it separated in orange-red balls, and melted at  $115-120^\circ$  to an orange-red syrup:

0.1108 gave 0.2286  $\text{CO}_2$  and 0.0469  $\text{H}_2\text{O}$ .  $\text{C}=56.1$ ;  $\text{H}=4.7$ .

0.1027 „ 8.6 c.c.  $\text{N}_2$  at  $14^\circ$  and 756 mm.  $\text{N}=9.8$ .

$\text{C}_{21}\text{H}_{25}\text{O}_4\text{N}$ ,  $\text{C}_8\text{H}_5\text{O}_7\text{N}_3$  requires  $\text{C}=55.5$ ;  $\text{H}=4.7$ ;  $\text{N}=9.6$  per cent.

This *picrate* was decomposed by warming with dilute ammonia, the base extracted with ether, the ethereal solution thoroughly washed, dried over potassium carbonate, and evaporated, when a syrup remained which, over phosphoric oxide in a vacuum desiccator, dried to a friable resin:

0.1271 gave 0.3292  $\text{CO}_2$  and 0.0817  $\text{H}_2\text{O}$ .  $\text{C}=70.6$ ;  $\text{H}=7.1$ .

$\text{C}_{21}\text{H}_{25}\text{O}_4\text{N}$  requires  $\text{C}=71.0$ ;  $\text{H}=7.0$  per cent.

*Dihydroanhydro-ψ-methylberberine* exhibits little tendency to crystallise, but it seems to become crystalline when left in a closed tube in contact with a little methyl alcohol. The hydrochloride is very readily soluble and gives, on the addition of platinic chloride, an ochreous, caseous precipitate of the *platinichloride* which, on warming, becomes chalky:

0.1217 gave 0.2040  $\text{CO}_2$  and 0.0521  $\text{H}_2\text{O}$ .  $\text{C}=45.7$ ;  $\text{H}=4.7$ .

0.2054 „ 0.0351 Pt.  $\text{Pt}=17.1$ .

$(\text{C}_{21}\text{H}_{25}\text{O}_4\text{N})_2, \text{H}_2\text{PtCl}_6$  requires  $\text{C}=45.1$ ;  $\text{H}=4.7$ ;  $\text{Pt}=17.3$  per cent.

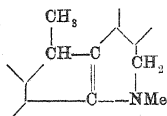
The addition of boiling dilute aqueous potassium iodide to the boiling dilute solution of the hydrochloride gave a milky liquid, from which a yellow syrup separated. This dissolved readily in methyl alcohol, and the solution, on spontaneous evaporation, deposited a crystalline mass of the *hydriodide*, which was drained on porous porcelain, dried in the steam-oven, and analysed:

0.1117 gave 0.2141  $\text{CO}_2$  and 0.0539  $\text{H}_2\text{O}$ .  $\text{C}=52.2$ ;  $\text{H}=5.3$ .

$\text{C}_{21}\text{H}_{25}\text{O}_4\text{N}, \text{HI}$  requires  $\text{C}=52.2$ ;  $\text{H}=5.4$  per cent.

### Section V.

*Derivatives of isoAnhydrocryptopine,*



The *isoanhydrocryptopine* required for these experiments was prepared by the method already given (1002), and certain direct derivatives of this substance, not previously described, were obtained during the course of the investigation.

*isoAnhydrocryptopine Methochloride*,  $\text{C}_{21}\text{H}_{31}\text{O}_4\text{N}, \text{MeCl}$ .—This characteristic derivative is readily obtained when *isoanhydrocryptopine* methiodide (1005), ground to a paste with much water, is digested on the steam-bath with excess of silver chloride for an hour. The filtrate, on concentration, deposits the methochloride as a hard crust of pale lemon-yellow prisms; after remaining exposed to the air until the weight was constant, this quaternary salt contained two molecules of water, and became opaque on drying at  $100^\circ$ :

1.7754 lost 0.1493 at  $100^\circ$ .  $\text{H}_2\text{O}=8.4$ .

$\text{C}_{21}\text{H}_{31}\text{O}_4\text{N}, \text{MeCl}, 2\text{H}_2\text{O}$  contains  $\text{H}_2\text{O}=8.2$  per cent.

0.1075 (dried at  $100^\circ$ ) gave 0.2577  $\text{CO}_2$  and 0.0575  $\text{H}_2\text{O}$ .  
 $\text{C}=65.4$ ;  $\text{H}=5.9$ .

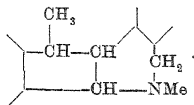
$\text{C}_{21}\text{H}_{31}\text{O}_4\text{N}, \text{MeCl}$  requires  $\text{C}=65.7$ ;  $\text{H}=6.0$  per cent.

*isoAnhydrocryptopine methochloride* melts at about  $233^\circ$  with vigorous decomposition to a black froth. It is very readily soluble in hot, but much less so in cold, water, and the addition of hydrochloric acid does not appear greatly to reduce the solubility. The aqueous solution gives no precipitate with ammonia or dilute sodium hydroxide.

The anhydrous salt dissolves readily in boiling methyl alcohol and separates, on cooling, in long, flat prisms which are quite colourless.

When the cold aqueous solution is mixed with dilute sulphuric acid and then a little manganese dioxide dusted in, a pale blue coloration gradually develops, which deepens on warming. The addition of dilute permanganate at  $0^{\circ}$  to the aqueous solution produces at first a purple precipitate of the permanganate, and then oxidation rapidly takes place.

*Dihydroisoanhydrocryptopine,*



This base was obtained by the reduction of *isoanhydrocryptopine* under the following conditions. The hydrochloride of *isoanhydrocryptopine*\* (1004) (3 grams), dissolved in dilute acetic acid and sodium acetate, was gradually treated with crushed sodium amalgam (200 grams of 3 per cent.) at about  $80^{\circ}$ . When the amalgam was exhausted, the filtered solution was mixed with ammonia, the chalky precipitate collected, and dissolved in hot dilute hydrochloric acid. On long keeping in the ice-chest, the very sparingly soluble *hydrochloride* of *dihydroisoanhydrocryptopine* separated, and was collected and recrystallised from dilute hydrochloric acid,† from which it separates in groups of colourless prisms; it darkens at  $210^{\circ}$  and decomposes at about  $215$ – $218^{\circ}$  with vigorous effervescence to an orange-red froth:

0.1101 gave 0.2619  $\text{CO}_2$  and 0.0625  $\text{H}_2\text{O}$ .  $\text{C}=64.5$ ;  $\text{H}=6.3$ .

$\text{C}_{21}\text{H}_{23}\text{O}_4\text{N}, \text{HCl}$  requires  $\text{C}=64.7$ ;  $\text{H}=6.2$  per cent.

This hydrochloride is comparatively readily soluble in hot water, but very sparingly so in dilute hydrochloric acid. The base, obtained by adding ammonia to the dilute aqueous solution of the hydrochloride, is a gelatinous precipitate becoming granular on warming, but all attempts to recrystallise the substance were unsuccessful. The precipitate, thoroughly washed, was dried over phosphoric oxide in a vacuum desiccator:

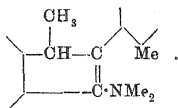
\* This hydrochloride, like that of anhydrocryptopine (977), is dissociated when sodium acetate is added to its aqueous solution.

† The mother liquors of this hydrochloride contain the hydrochloride of a second base which also has the composition  $\text{C}_{21}\text{H}_{23}\text{O}_4\text{N}$ , and it is probable that the two bases represent stereoisomeric modifications of the same substance.

0.1070 gave 0.2801  $\text{CO}_2$  and 0.0621  $\text{H}_2\text{O}$ .  $\text{C}=71.2$ ;  $\text{H}=6.4$ .

$\text{C}_{21}\text{H}_{23}\text{O}_4\text{N}$  requires  $\text{C}=71.4$ ;  $\text{H}=6.5$  per cent.

Section V (a). *The Reduction of isoAnhydrocryptopine Methosulphate in Alkaline Solution* (p. 732): *Formation of Dihydromethylisoanhydrocryptopine, (A) and (B),*



The isoanhydrocryptopine methosulphate used in these experiments was prepared by adding methyl sulphate to the benzene solution of isoanhydrocryptopine in the manner already described (1005). The carefully purified substance (5 grams), dissolved in boiling water (300 c.c.), was vigorously stirred with crushed sodium amalgam (150 grams of 3 per cent.), when a base separated, sometimes in crystalline form, but more frequently as a gum, which ultimately crystallised. The whole was heated on the steam-bath until no further separation could be observed; the base was then collected, washed well, dried on porous porcelain, and dissolved in boiling methyl alcohol. When this solution is allowed to remain without agitation, the modification (A) of dihydromethylisoanhydrocryptopine separates as a bulky mass of soft needles, but gradually pale yellow prisms of the modification (B) make their appearance, and, if the hot solution is stirred during crystallisation, the separation consists entirely of this modification. The prisms (B) melt sharply at  $121-122^\circ$ , but, when the needles (A) are slowly heated in a capillary tube, it is noticed that they sinter at about  $105^\circ$ , clearly owing to transition into the prismatic modification, and the melting point is again  $121-122^\circ$ . Both modifications were analysed:

(A) 0.1098 gave 0.2908  $\text{CO}_2$  and 0.0687  $\text{H}_2\text{O}$ .  $\text{C}=72.2$ ;  $\text{H}=7.0$ .

(B) 0.1101 gave 0.2906  $\text{CO}_2$  and 0.0685  $\text{H}_2\text{O}$ .  $\text{C}=72.0$ ;  $\text{H}=6.9$ .

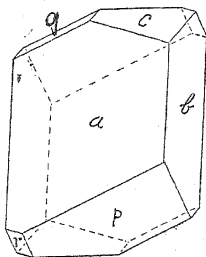
$\text{C}_{22}\text{H}_{25}\text{O}_4\text{N}$  requires  $\text{C}=71.0$ ;  $\text{H}=6.8$  per cent.

Crystals of this substance were kindly examined by Miss M. W. Porter, who reports that the system is anorthic, with  $a:b:c=0.728:1.0766$ ,  $\alpha=100^\circ 15'$ ,  $\beta=104^\circ 23'$ ,  $\gamma=95^\circ 2'$ . The following forms were observed:  $b(010)$ ,  $a(100)$ ,  $c(001)$ ,  $q(0\bar{1}1)$ ,  $r(\bar{1}01)$ , and  $p(\bar{1}\bar{1}1)$ . The habit, as is shown in Fig. 4, is prismatic, and the

vertical faces are generally curved. Following are the mean measurements derived from three crystals:

	Azimuth.	Polar distance.
<i>b</i> (010)	0° 0'	90° 0'
<i>a</i> (100)	*82 2	90 0
<i>c</i> (001)	*49 33	*18 37
<i>q</i> (011)	155 8	32 25
<i>r</i> (101)	275 24	39 25
<i>q</i> (111)	*229 4	*47 42

FIG. 4.



*Dihydromethylisoanhydrocryptopine* (B), m. p. 122°.

The solution of a trace of either modification in a drop of acetic acid gives with sulphuric acid a deep orange-red coloration, which becomes intense port wine and then brown on the addition of dilute nitric acid. *Dihydromethylisoanhydrocryptopine* is very readily soluble in cold dilute hydrochloric acid, but, on rubbing, the sparingly soluble crystalline hydrochloride immediately separates. This fine salt is readily soluble in hot water, and crystallises in short, six-sided prisms with obliquely cut-off ends. The sulphate does not crystallise under these conditions, but the addition of dilute nitric acid to the solution of the sulphate causes the nitrate to separate as a syrup, which crystallises on rubbing.

*The Methosulphate.*—This characteristic derivative is readily prepared by adding methyl sulphate (3 c.c.) to the solution of the base (2.5 grams) in a little warm benzene, when combination takes place immediately with the evolution of much heat. The liquid soon becomes a pasty mass of crystals, and these are collected, washed with benzene, and recrystallised from water or methyl alcohol:

0.1094 gave 0.2334 CO<sub>2</sub> and 0.0623 H<sub>2</sub>O. C=58.2; H=6.3.

C<sub>22</sub>H<sub>25</sub>O<sub>4</sub>N, Me<sub>2</sub>SO<sub>4</sub> requires C=58.4; H=6.3 per cent.



*Dihydromethylisoanhydrocryptopine methosulphate* melts at about  $202^{\circ}$ , without effervescence, to a colourless syrup, and is readily soluble in hot water, from which it separates in groups of flat needles; the aqueous solution gives no precipitate on the addition of ammonia. It dissolves very readily in boiling methyl alcohol, but is much less soluble in the cold and separates in thin plates with obliquely cut-off ends. When warmed with methyl-alcoholic potassium hydroxide (15 per cent.), it dissolves, and, on boiling, decomposition slowly sets in with the elimination of trimethylamine; the liquid becomes brown, then deep purple, and finally nearly black, and the addition of water then precipitates a black substance (compare 985).

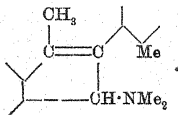
*The Methiodide.*—The addition of hot dilute potassium iodide to the hot dilute solution of the methosulphate produces no immediate precipitate, but the liquid soon clouds, and a gum separates which, on rubbing, readily crystallises. If this gum is dissolved in boiling alcohol and the solution stirred, the methiodide separates as a sandy precipitate consisting of curious, circular warts:

0.1121 gave 0.2215  $\text{CO}_2$  and 0.0563  $\text{H}_2\text{O}$ .  $\text{C}=53.9$ ;  $\text{H}=5.6$ .

$\text{C}_{23}\text{H}_{25}\text{O}_4\text{N}, \text{MeI}$  requires  $\text{C}=54.2$ ;  $\text{H}=5.5$  per cent.

This *methiodide* melts at about  $215\text{--}217^{\circ}$  to a yellow syrup.

*$\psi$ -Dihydromethylisoanhydrocryptopine* (p. 732),



This substance is obtained (a) from *isoanhydrocryptopine* methochloride (p. 780) by reduction in hydrochloric acid solution with sodium amalgam, or (b) from *dihydromethylisoanhydrocryptopine* by boiling with dilute hydrochloric acid. (a) *isoAnhydrocryptopine* methochloride (3 grams), dissolved in hot water (200 c.c.) and hydrochloric acid (30 c.c.), is treated with sodium amalgam (120 grams of 4 per cent.) on the steam-bath. When reduction is complete, the liquid is filtered from a trace of a chalky, neutral substance, the filtrate mixed with ammonia, the rather gelatinous precipitate collected, washed, dried on porous porcelain, and dissolved in a little boiling methyl alcohol, in which it is very readily soluble. If the solution is cooled in ice and salt and rubbed, crystallisation gradually sets in, and, on recrystallisation, pure  *$\psi$ -dihydromethylisoanhydrocryptopine* is obtained in colourless needles melting at

140—141°. (b) Dihydromethylisoanhydrocryptopine (1 gram), dissolved in concentrated hydrochloric acid (2 c.c.) and water (10 c.c.), is boiled for ten minutes in an open test-tube by means of a sulphuric-acid bath in such a way that concentration to about half the volume takes place. At first there is no visible change, but towards the end of the operation a pale green develops. The cold product yields a caseous precipitate on the addition of ammonia, which soon becomes hard, and the substance separates from methyl alcohol in microscopic groups of needles melting at 140—141°. Analyses were made with substances prepared by methods (a) and (b):

(a) 0.1238 gave 0.3271  $\text{CO}_2$  and 0.0776  $\text{H}_2\text{O}$ .  $\text{C}=72.0$ ;  $\text{H}=6.9$ .

(b) 0.1250 „ 0.3298  $\text{CO}_2$  „ 0.0783  $\text{H}_2\text{O}$ .  $\text{C}=71.9$ ;  $\text{H}=6.9$ .

$\text{C}_{22}\text{H}_{25}\text{O}_4\text{N}$  requires  $\text{C}=71.9$ ;  $\text{H}=6.8$  per cent.

*$\psi$ -Dihydromethylisoanhydrocryptopine* is sparingly soluble in cold methyl alcohol and not very readily so on boiling; it is also rather sparingly soluble in cold acetone, but dissolves on boiling and separates in groups of glistening needles; it is easily soluble in benzene, even in the cold. The solution of a crystal in a drop of acetic acid gives, with sulphuric acid, a deep orange coloration, which becomes intense port wine on the addition of a drop of dilute nitric acid. A characteristic of the base is its remarkable resistance to reduction, since experiment showed that much remains unchanged after its solution in dilute hydrochloric acid has been boiled with a large excess of sodium amalgam (compare p. 733).

It is also oxidised with unusual difficulty when permanganate is added to its solution in acetone.

*The Methosulphate*.—A considerable rise of temperature takes place when methyl sulphate is added to the solution of the base in warm benzene, and the methosulphate begins to separate immediately as a chalky mass. This was collected, washed with benzene, and analysed:

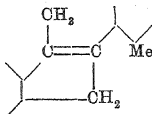
0.1092 gave 0.2332  $\text{CO}_2$  and 0.0626  $\text{H}_2\text{O}$ .  $\text{C}=58.1$ ;  $\text{H}=6.4$ .

$\text{C}_{22}\text{H}_{25}\text{O}_4\text{N}, \text{Me}_2\text{SO}_4$  requires  $\text{C}=58.4$ ;  $\text{H}=6.3$  per cent.

*$\psi$ -Dihydromethylisoanhydrocryptopine methosulphate* melts at about 188—190°, and is sparingly soluble in water or methyl alcohol in the cold, but dissolves readily on warming and separates in colourless groups of needles. It is decomposed with some difficulty by boiling methyl-alcoholic potassium hydroxide (15 per cent.), trimethylamine is eliminated, and, on the addition of water, a chalky substance separates, which was not further examined.

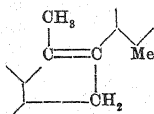
*Reduction of the Methosulphate*.—When crushed sodium amalgam was added to the cold aqueous solution of the metho-

sulphate at about  $50^{\circ}$ , the odour of trimethylamine became at once apparent, and a chalky substance separated. After keeping at  $50^{\circ}$  for some hours, with constant stirring, the precipitate was collected, and found to melt at  $160$ — $163^{\circ}$ . It was recrystallised from methyl alcohol, in which it was remarkably sparingly soluble, and then melted at  $166$ — $167^{\circ}$ . That this substance is *isocryptopidene* (A),



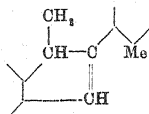
that is to say, is identical with the substance which results from the cold reduction of dihydromethylisoanhydrocryptopine methosulphate (see below), was proved by a comparison of properties, and particularly by the fact that the mixture of the two substances melted at  $166$ — $167^{\circ}$ .

*The isocryptopidenes, (A) and (B),*



(A.) M. p.  $167^{\circ}$ .

and



(B.) M. p.  $108^{\circ}$ .

The difficulty of completely understanding the mechanism of the formation of these curious and interesting substances is referred to in the introduction to this paper (p. 733), and reasons are there given for assigning the above formulæ to the two isomerides.

*isocryptopidene* (A) (m. p.  $167^{\circ}$ ) is produced by the reduction (i) of the methosulphate of dihydromethylisoanhydrocryptopine, or (ii) of the methosulphate of  $\psi$ -dihydromethylisoanhydrocryptopine in alkaline solution and also by the reduction of  $\psi$ -dihydromethylisoanhydrocryptopine in acid solution. The method of formation (ii) has just been described, but the method of preparation which is probably most convenient is that stated under (i). In this reduction, dihydromethylisoanhydrocryptopine methosulphate (2 grams, p. 783), dissolved in water (150 c.c.), is poured on freshly prepared crushed sodium amalgam (100 grams of 3 per cent.) in a porcelain beaker fitted with a mechanical stirrer, and the reduction carried out at a temperature not exceeding  $30^{\circ}$ . The odour of trimethylamine becomes immediately apparent, and a chalky precipitate of *iso-*

cryptopidene (4) gradually forms, but the separation is not complete until the stirring has been continued for two days. The precipitate is then collected, washed with water, and dried in the steam-bath, when it melts at 163—165°, and is almost pure *iso*-cryptopidene (4), the yield being very good. For analysis, the substance was recrystallised from much methyl alcohol, and considerable difficulty was experienced in obtaining accurate results:

0.1195 gave 0.3231 CO<sub>2</sub> and 0.0654 H<sub>2</sub>O. C=73.7; H=6.1.

0.1075 „ 0.2901 CO<sub>2</sub> „ 0.0584 H<sub>2</sub>O. C=73.6; H=6.0.

C<sub>20</sub>H<sub>20</sub>O<sub>4</sub> requires C=74.1; H=6.2 per cent.

*isoCryptopidene* (4) melts at 166—167°, and is remarkably sparingly soluble in boiling methyl alcohol, from which it separates as a sandy powder consisting of well-developed, glistening prisms; it is also very sparingly soluble in boiling alcohol or acetone, and separates from the latter in striated prisms. The solution of a crystal in a few drops of glacial acetic acid gives with sulphuric acid a deep orange coloration, which changes to red on the addition of a drop of nitric acid.

(iii) *The Reduction of ψ-Dihydromethylisoanhydrocryptopine* (p. 784) *in Acid Solution*.—In carrying out this experiment dihydromethylisoanhydrocryptopine (5 grams) (m. p. 122°, p. 782) was dissolved in a large excess of boiling dilute hydrochloric acid, and thus converted into the *ψ*-isomeride (p. 785). Freshly prepared sodium amalgam (250 grams of 4 per cent.) was then added to the boiling solution, when a small amount of a chalky precipitate separated, which was collected, washed well, and dried in the steam-oven. In this condition, it melted at 162—165°, and, after recrystallisation from methyl alcohol, in which it was very sparingly soluble, at 166—167°. The careful comparison of the properties of this substance with those of the specimen of *isocryptopidene* (4) obtained from the alkaline reduction of dihydromethylisoanhydrocryptopine methosulphate (see above) clearly indicated identity, and this was confirmed by the observation that the mixture of the two preparations melted at 166—167°.

The yield of *isocryptopidene* (4) obtained by reducing *ψ*-dihydromethylisoanhydrocryptopine in acid solution is only about 8 per cent. of that theoretically possible, and this led to a careful examination of the acid solution which had been separated from the neutral substance by filtration. On the addition of ammonia, a caseous precipitate separated, which soon hardened, and when rubbed with methyl alcohol this yielded a sparingly soluble substance (a), which was collected and washed with a little methyl alcohol to remove a readily soluble substance (b). The

substance (a) on fractional crystallisation from methyl alcohol was separated into, a small quantity of a new base (m. p. 168—170°) and a considerable quantity (0·8 gram) of unreduced  $\psi$ -dihydro-methylisoanhydrocryptopine (m. p. 140°). In view of the fact that reduction had been carried out at the boiling point and with a very large excess of amalgam, it is remarkable that so much of this base should have remained unreduced. The base melting at 168—170° is very sparingly soluble in boiling methyl alcohol, from which it separates as a voluminous mass of colourless needles. The solution in acetic acid is coloured yellowish-brown by sulphuric acid, and the addition of a drop of dilute nitric acid changes the colour to brownish-pink:

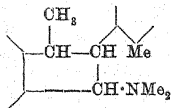
0·1077 gave 0·2853 CO<sub>2</sub> and 0·0662 H<sub>2</sub>O. C=72·1; H=6·8.

C<sub>22</sub>H<sub>25</sub>O<sub>4</sub>N requires C=71·9; H=6·8 per cent.

This analysis shows that the base is isomeric with dihydro-methylisoanhydrocryptopine (m. p. 122°) and  $\psi$ -dihydromethylisoanhydrocryptopine (m. p. 140°), but no evidence is available to explain this isomerism.

The methyl-alcoholic filtrate from the substance (b) was mixed with much ether, the ethereal solution washed until quite free from methyl alcohol, dried over potassium carbonate, concentrated, and left in the ice-chest for a week, during which it deposited a small crop of the base melting at 140°, which is practically insoluble in ether.

As no further separation took place on allowing the ether to evaporate in the ice-chest, the base was dissolved in dilute hydrochloric acid and precipitated with ammonia, when a caseous mass separated which, after drying over phosphoric oxide in a vacuum desiccator, gave numbers indicating that the base is *tetrahydro-methylisoanhydrocryptopine*,



0·1139 gave 0·2969 CO<sub>2</sub> and 0·0753 H<sub>2</sub>O. C=71·0; H=7·5.

C<sub>22</sub>H<sub>27</sub>O<sub>4</sub>N requires C=71·5; H=7·3 per cent.

This base is very readily soluble in the usual solvents, and all attempts to obtain it in a crystalline condition were unsuccessful. The solution in benzene becomes hot on the addition of methyl sulphate, clouds, and a syrup separates which hardens when rubbed with ether. This methosulphate, which is very readily soluble in

water or methyl alcohol, yields a heavy syrup on the addition of boiling potassium iodide to its hot aqueous solution. On remaining in the ice-chest, this gradually deposited nodular crystals, and, when rubbed with methyl alcohol, a considerable quantity of a white, crystalline substance separated, which was collected and recrystallised from methyl alcohol.

*Tetrahydromethylisoanhydrocryptopine methiodide* melts without effervescence at about  $188-190^{\circ}$  to a viscid, pale yellow syrup, is comparatively readily soluble in boiling methyl alcohol, but very sparingly so in the cold, and separates well as a glistening mass consisting of thin, flat plates with square ends:

0.1201 gave 0.2390  $\text{CO}_2$  and 0.0641  $\text{H}_2\text{O}$ .  $\text{C}=54.3$ ;  $\text{H}=6.0$ .

$\text{C}_{22}\text{H}_{27}\text{O}_4\text{N}, \text{MeI}$  requires  $\text{C}=54.0$ ;  $\text{H}=5.8$  per cent.

*isoCryptopidine (B)* (m. p.  $108^{\circ}$ ).—This substance is obtained when the methosulphate of dihydromethylisoanhydrocryptopine (3 grams) (p. 783), dissolved in boiling water (150 c.c.), is treated with sodium amalgam (150 grams of 3 per cent.), care being taken to keep the whole boiling during the operation. Immediately the amalgam is added, a syrupy substance begins to separate, and, if the mass is vigorously stirred, the reduction is finished in a few minutes. The syrupy substance, which crystallises on cooling, is collected and recrystallised from alcohol:

0.1291 gave 0.3497  $\text{CO}_2$  and 0.0701  $\text{H}_2\text{O}$ .  $\text{C}=73.9$ ;  $\text{H}=6.1$ .

$\text{C}_{20}\text{H}_{20}\text{O}_4$  requires  $\text{C}=74.1$ ;  $\text{H}=6.2$  per cent.

*isoCryptopidine (B)* melts at  $108^{\circ}$ , is more readily soluble in methyl or ethyl alcohol than the modification (A), and separates in groups of glistening needles. It is readily soluble in benzene or acetone in the cold, or in boiling glacial acetic acid, and crystallises particularly well from 70 per cent. acetic acid as a voluminous mass of needles. The solution of a trace in glacial acetic acid gives with sulphuric acid a deep orange-red coloration, which becomes redder on the addition of a drop of dilute nitric acid.

*Oxidation*.—The solution of the substance (3 grams) in acetone (200 c.c.) is slowly oxidised by the addition of very finely powdered permanganate (5 grams) at the ordinary temperature, the operation requiring about five hours. The manganese precipitate was collected, washed with acetone, extracted with boiling water, and the brown extract concentrated and acidified, when an ochreous precipitate separated in quantity, and was washed and left in contact with porous porcelain until dry. The whole was then dissolved in boiling methyl alcohol and allowed to remain in the ice-chest for two days, when a crystalline acid (0.25 gram) had

separated; this was recrystallised from methyl alcohol, in which it is very sparingly soluble:

0.1060 gave 0.2391  $\text{CO}_2$  and 0.0460  $\text{H}_2\text{O}$ .  $\text{C}=61.5$ ;  $\text{H}=4.9$ .

$\text{C}_{20}\text{H}_{20}\text{O}_8$  requires  $\text{C}=61.5$ ;  $\text{H}=5.1$  per cent.

This acid, which may be called *ketohydroxydihydroisocryptopidenic acid*, and the possible constitution of which is discussed on p. 734, is a colourless, satiny mass; it becomes salmon-coloured at  $220^\circ$  and melts at  $227^\circ$  without effervescence.

The solution in concentrated methyl-alcoholic potassium hydroxide becomes pink on boiling, and the colour gradually fades in contact with air.

A trace dissolved in a drop of acetic acid gives with sulphuric acid a deep brown coloration which, on the addition of a drop of dilute nitric acid, gradually fades. The methyl-alcoholic mother liquors of this acid contain a considerable quantity of readily soluble acids, and the acetone extract from the oxidation yields, on evaporation, a small quantity of a yellow syrup, but no attempt was made to identify these mixtures of substances.

The considerable quantities of cryptopine required for this investigation were collected for me by Messrs. T. and H. Smith, of Edinburgh, and I wish again to thank the firm and the managing director, Dr. Alexander Dey, for the generous assistance they have extended to me throughout this inquiry. I am also indebted to Mr. T. V. Barker and Miss M. V. Porter for undertaking the crystallographic measurement of some of the new derivatives. The analyses were again carried out by Mr. Fred Hall with characteristic skill.

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## LXI.—*The Freezing Point of Solutions, with Special Reference to Solutions Containing Several Solutes.*

By CHARLES EDWARD FAWSITT.

IN proceeding to use freezing-point determinations for the estimation of certain ingredients in liquids containing an unlimited number of ingredients, the author found that it was necessary to consider rather closely the freezing points of solutions. In particular, for the purpose in question, it was necessary to consider

how the calculated molecular depression of the freezing point of a solvent by a solute is dependent on the concentration of the solute (Part I), and it was necessary further to consider what effect is produced on the freezing point of a solvent by several solutes used together, as compared with the effect of these solutes used separately (Part II).

These two matters are considered in this paper.

## PART I.

### *The Effect of Concentration of Solute in Freezing-point Determinations.*

The freezing point of a solvent is usually lowered by dissolving any substance in it, and for very dilute solutions the depression of the freezing point, ( $\Delta$ ), is proportional to  $n/N$ , where  $n$  is the number of solute molecules and  $N$  is the number of solvent molecules.

This proportionality is proved from theoretical considerations, but holds only for excessively dilute solutions. For solutions of a concentration of, say, 1—10 per cent. of solute,  $\Delta$  is not strictly proportional to  $n/N$ , and it has been suggested that the formula

$$\Delta \propto \frac{n}{N+n}$$

should be used instead of

$$\Delta \propto \frac{n}{N}$$

Taking the first formula, which is more commonly used,

Let  $w$  = weight in grams of solute,

$m$  = molecular weight of solute,

$W$  = weight of solvent in grams,

$M$  = molecular weight of solvent,

$$\Delta \propto \frac{w}{m} \times \frac{M}{W},$$

or

$$\Delta = K \times 1000 \times \frac{w}{m} \times \frac{1}{W} \dots \dots (1)$$

where  $K$  is a constant (the van't Hoff constant) for the solvent and represents the depression caused by introducing one gram-molecular weight of solute into 1000 grams of solvent.

Equation (1) is usually employed in making freezing-point calculations, more especially where these are used in determining molecular weights of solutes.



It is observed that when the depressions  $\Delta_1$ ,  $\Delta_2$ ,  $\Delta_3$ , corresponding with several weights of solute,  $w_1$ ,  $w_2$ ,  $w_3$ , are determined, the molecular weight of the solute, calculated according to equation (1), is often not constant, even with non-associated or non-dissociated solutes. In such cases, the numbers more often tend to rise than to fall.

It might be thought that by using the formula

$$\Delta \propto \frac{n}{N+n}$$

instead of

$$\Delta \propto \frac{n}{N}$$

better results would be obtained.

Now

$$\Delta \propto \frac{n}{N+n}$$

leads to

$$\Delta \propto \frac{M \cdot w}{[m \cdot W + wM]}$$

or

$$\Delta = K \times 1000 \cdot \frac{w}{m[W + w/m \cdot M]} \quad \dots \quad (2)$$

where  $K$  is the same constant as in (1). The application of equation (2) to the calculation of molecular weights instead of (1) is not attended by satisfactory results.

In particular, it cannot be made to serve any useful purpose when the molecular weights, calculated according to (1), decrease as the concentration rises, a case which sometimes occurs.

If, however, instead of the expression in (2) we use the formula

$$\Delta = \frac{K \times 1000 \times w}{m[W + bw]} \quad \dots \quad (3)$$

where  $b$  is an arbitrarily introduced constant dependent on solute and solvent, not necessarily equal to  $M/m$ , and, indeed, sometimes negative, the results obtained are satisfactory.

Abegg (*Zeitsch. physikal. Chem.*, 1894, 15, 209) tried the equation

$$\Delta = \frac{K \times n \times 1000}{W} + B \left( \frac{n}{W} \right)^2 \quad \dots \quad (4)$$

where  $K$  is the ordinary van't Hoff constant as used in equation (1), and should be the same for all solutes in any particular solvent, whilst  $B$  is an arbitrary constant which varies with the solute. The application of this formula (4) certainly gives better results

in many cases than (1) or (2), but is not so simple a formula as (3). The latter gives quite as good results as (4) both for solutions containing a single solute and solutions containing several solutes.

The author considers that formula (3) is the most suitable for adoption in freezing-point calculations.

The constant  $b$  in equation (3) can be calculated from two observations; if  $w_1$  and  $w_2$  be two different weights of a solute giving depressions  $\Delta_1$  and  $\Delta_2$  with a particular solvent, then

$$b = \frac{W(\Delta_1/w_1 - \Delta_2/w_2)}{\Delta_2 - \Delta_1}.$$

The constant  $B$  in equation (4) can also be calculated from two observations,

$$B = \frac{W^2(\Delta_1/w_1 - \Delta_2/w_2)}{w_1 - w_2}.$$

In the following tables,  $m$  is the (theoretical) molecular weight,  $m'$  is the molecular weight as calculated by the equation

$$m' = \frac{K \cdot 1000 \cdot w}{\Delta \cdot W} \quad \dots \quad (5)$$

$m''$  is the molecular weight as calculated by the equation

$$m'' = \frac{K \cdot 1000 \cdot w}{\Delta \cdot [W + bw]} \quad \dots \quad (6)$$

$m'''$  is the molecular weight as calculated by the equation

$$m''' = \frac{K \cdot 1000 \cdot w}{W[\Delta - B \cdot w^2/W^2]} \quad \dots \quad (7)$$

which is derived from equation (4).

From tables I, II, III, and IV it will be seen that  $m''$  is fairly constant whether  $m'$  rises or falls with increasing concentration of solute.

In table II,  $m'''$  is also given, and it will be seen that it is just as constant as  $m''$ , but not more so.

TABLE I.

*Solute, Ethyl Ether,  $m=74$ ; Solvent, Cineole.*  
 $W=18.27$ ,  $b=1.53$ ,  $K=6.7$ .

Grams of solute in 100 grams of solvent.	$\Delta$ .	$m'$ (calculated).	$m''$ .
0.707	0.624	76.0	75.1
1.48	1.275	77.6	75.9
2.2	1.875	78.5	76.0
3.4	2.874	79.3	75.2
5.15	4.255	81.0	75.1

TABLE II.

*Solute, 1- $\alpha$ -Phellandrene,  $m=136$ ; Solvent, Benzene.* $B = -33.6$ ,  $W = 18.47$ ,  $b = 0.87$ ,  $K = 5.0$ .

$w \times 100/W$ .	$\Delta$ .	$m'$ .	$m''$ .	$m'''$ .
0.96	0.356	135.2	133.9	133.9
2.12	0.778	136.5	133.9	133.7
3.32	1.194	138.9	134.9	134.6
4.7	1.685	140.4	134.7	134.3
6.24	2.209	141.2	133.8	133.1
7.34	2.559	143.3	134.7	133.8

The variations in  $m''$  (and  $m'''$ ) of the tables are not greater than the experimental errors.

Tables of this kind could be multiplied indefinitely.

Tables III and IV give examples where  $b$  has a negative value (that is, where the molecular weight as calculated from equation (1) falls with increasing concentration). Table III has been calculated from data given by Abegg (*loc. cit.*).

TABLE III.

*Solute, Ethyl Alcohol; Solvent, Water.* $K = 1.86$ ,  $W = 100$ ,  $m = 46$ ,  
 $b = -0.5$ .

$w$ .	$\Delta$ .	$m'$	$m''$
8.10	3.215	46.8	48.8
10.75	4.35	46.0	48.6
13.81	5.605	45.8	49.2
17.79	7.49	44.6	49.2
22.50	9.705	43.1	48.5
32.68	15.09	40.2	48.1

TABLE IV.

*Solute, Sucrose; Solvent, Water.* $K = 1.86$ ,  $W = 100$ ,  $m = 342$ ,  
 $b = -0.26$ .

$w$ .	$\Delta$ .	$m'$	$m''$
0.973	0.053	341.4	342.3
2.231	0.123	337.4	339.3
4.276	0.237	335.6	339.4
8.550	0.481	330.7	338.2
17.292	0.989	325.1	340.2

In table III it will be seen that  $m''$  is constant within the experimental error up to a concentration of 32.68\* per cent. of solute.

Table IV is calculated from data given by Raoult (1898).

When the molecular weight as calculated according to equation (5) rises with increasing concentration, this is due probably (i) to the volume of the solution becoming continually greater than the volume of the solvent, or (ii) to association of the solute molecules.

When the molecular weight as calculated according to (5) falls with increasing concentration, this is due probably to combination between solute and solvent.

Whatever be the cause of the rising or falling of the calculated molecular weight, there seems to be little doubt that where the molecular weight calculated according to (5) rises or falls with

change of concentration, formula (6) gives values for  $m''$  constant to about 1 per cent. This is, then, the calculated value of the molecular weight for very small concentrations. It does not immediately follow that this constant value ( $m''$ ) represents accurately the true molecular weight ( $m$ ), for there are other abnormalities noticed in the results of freezing-point measurements besides the rising and falling of the (calculated) molecular weight. The molecular weight as calculated for small concentrations may be higher or lower than the true molecular weight. It is higher in the case of many solutes showing association, for example, ethyl alcohol dissolved in cineole. It is also sometimes lower than the true molecular weight; this is more particularly noticeable in the case of some terpenes dissolved in benzene and in cineole.

## PART II.

*Freezing Point of a Mixture of Solutes Dissolved in a Solvent.*

In proceeding to the case of several solutes dissolved together in a solvent, it will be desirable to eliminate certain complications.

For example, it is not desirable to use as solutes in the mixture, (i) such solutes as exhibit association or dissociation in solution, (ii) such as will form mixed crystals with the solvent, (iii) such as will combine with the solvent or with each other.

In some cases, a fairly close agreement is observed between the depression of the freezing point, caused by a mixture of solutes, and the sum of the depressions, caused by the ingredients when introduced by themselves (separately) into the solvent.

TABLE V.

*Solvent, Benzene; Solute, Toluene.*

$W=18.65$ ,  $K=5.0$ .

$W$	Percentage of solute.	$\Delta$ .
0.1822	0.98	0.542
0.3522	1.89	1.017
0.6866	3.68	2.028

TABLE VI.

*Solvent, Benzene; Solute, p-Xylene.*

$W=15.092$ ,  $K=5.0$ .

$w$	$w \times 100/W$ .	$\Delta$ .
0.2306	1.53	0.750
0.5224	3.46	1.626
0.8151	5.40	2.542

In table VII and the following tables,  $\Delta_1$  is the depression of the freezing point of a mixture of solutes in a solvent obtained by adding together the calculated depressions of the freezing point caused by each ingredient.  $\Delta$  is the observed depression.

TABLE VII.

*Solvent, Benzene; Solute, a Mixture containing 84.7 per cent. of Toluene and 15.3 per cent. of p-Xylene.*

$$W = 15.29.$$

<i>w.</i>	$\Delta$ .	$\Delta_1$ .
0.1887	0.670	0.648
0.3663	1.274	1.268
0.615	2.114	2.139

The calculated and observed depressions do not differ by much more than the experimental errors in this case.

However, if a considerable number of cases are examined, using various solutes and solvents, it will be found that there is often a considerable discrepancy between the values of  $\Delta$  and  $\Delta_1$ , especially at large concentrations; sometimes  $\Delta$  is greater than  $\Delta_1$ , sometimes less. This is, however, only to be expected from equation (3).

From equation (3) we are led to believe that, instead of using  $W$ , the weight of pure solvent, in our calculations, we should use  $W + bw$ .

Consider now two solutes,  $P$  and  $Q$ , having molecular weights  $m_p$  and  $m_q$ ; let  $w_p$  grams of  $P$  be dissolved in a solvent, giving a depression  $\Delta_p$ ; let  $w_q$  grams of  $Q$  when dissolved (separately) in the solvent give a depression  $\Delta_q$ .

Then the separate depressions are:

$$\Delta_p = \frac{K \cdot 1000 \cdot w_p}{m_p \cdot [W + b_p w_p]} \quad \text{and} \quad \Delta_q = \frac{K \cdot 1000 \cdot w_q}{m_q [W + b_q w_q]}$$

and the sum

$$\Delta_p + \Delta_q = K \cdot 1000 \left\{ \frac{w_p/m_p}{[W + b_p w_p]} + \frac{w_q/m_q}{[W + b_q w_q]} \right\} \quad (8)$$

The sum  $\Delta_p + \Delta_q$  differs from the observed value  $\Delta_{p+q}$  since the observed value would be expected to be given by

$$\Delta_{p+q} = \frac{K \cdot 1000 \{w_p/m_p + w_q/m_q\}}{[W + b_p w_p + b_q w_q]} \quad (9)$$

If  $b_p$  and  $b_q$  are positive, then  $\Delta_{p+q}$  will be less than  $\Delta_p + \Delta_q$ . If  $b_p$  and  $b_q$  are negative, then  $\Delta_{p+q}$  will be greater than  $\Delta_p + \Delta_q$ . We may say then, in general, that on mixing two solutes the molecular weights of which when calculated according to the usual formula (equation 5) rise with increasing concentration ( $b + w$ ), we should expect that the actual depression produced by the two

together would be less than the sum of the depressions produced by each solute separately.

If, on the other hand, the molecular weights when calculated according to equation (5) decrease with increasing concentration ( $b$  negative), we should expect that the depression produced by two solutes together would be greater than the sum of the depressions of the separate solutes.

An examination of a considerable number of cases shows that, qualitatively, these statements are borne out by facts.

It is assumed, of course, in such cases that there is no combination between the various solutes. This would itself have the effect of making the observed less than the calculated depression.

Below are given the results of a number of freezing-point determinations on single solutes in benzene showing how the molecular weight, calculated according to equation (5), alters with change of concentration, and, subsequently, tables showing the results obtained from mixtures of some of these solutes in benzene.

Results for mixtures of solutes are given for the three solvents benzene, nitrobenzene, and water.

$\Delta_2$  in the following tables denotes the calculated depression as obtained from equation (9).

$m'$  is calculated from equation (5).

Percentage of solute means weight of solute in 100 grams of solvent.

#### *Benzene as Solvent.*

The following results were obtained with individual solutes.

TABLE VIII.

*Solvent, Benzene; Solute, Toluene.*

$K=5$ ,  $m=92$ .

Percentage weight of solute.	$\Delta$ .	$m'$ .
1.467	0.847	86.6
3.088	1.754	88.1
4.715	2.588	91.1
6.205	3.338	93.0
7.803	4.148	94.1

$b$  Calculated from these figures is 1.312.

TABLE IX.

*Solvent, Benzene; Solute, m-Xylene.*

$m=106$ .

Percentage weight of solute.	$\Delta$ .	$m'$ .
1.189	0.568	104.7
2.674	1.253	106.7
4.111	1.881	109.3
5.595	2.526	110.8
6.773	3.014	112.4

$b$  Calculated from these figures is 1.339.

TABLE X.

*Solvent, Benzene; Solute,*  
*d-Pinene.**m* = 136.

Percentage.	$\Delta$ .	$m$ .
1.411	0.54	130.6
2.823	1.032	136.9
4.438	1.564	141.9
6.193	2.15	144.1

*b* Calculated from observations (1)  
and (4) is 2.21.

TABLE XI.

*Solvent, Benzene; Solute,*  
 *$\alpha$ -Phellandrene.**m* = 136.

Percentage.	$\Delta$ .	$m'$ .
0.962	0.356	135.2
2.123	0.778	136.5
3.316	1.194	138.9
4.731	1.685	140.4
6.236	2.209	141.2
7.335	2.559	143.3

*b* Calculated from observations (1)  
and (6) is 0.87.

TABLE XII.

*Solvent, Benzene; Solute, Cineole.**m* = 154.

Percentage.	$\Delta$ .	$m'$ .
1.046	0.350	149.4
2.708	0.870	155.7

*b* Calculated from observations (1) and (2) is 2.59.

TABLE XIII.

*Freezing-point Determinations with more than One Solute in*  
*Benzene as Solvent. Solvent, Benzene (*K* = 5.0).*

No.	Solute.	* Value of " <i>b</i> " for solute.	Percentage weight of solute.	$\Delta$ .	$\Delta_1$ .	$\Delta_2$ .	Percentage difference between $\Delta$ and $\Delta_1$ .
1	Toluene .....	1.312	2.368	1.569	1.604	1.588	1.2
	<i>m</i> -Xylene ...	1.339	0.532				
2	Toluene .....	1.312	3.759	2.469	2.508	2.466	-0.1
	<i>m</i> -Xylene ...	1.339	0.845				
3	Toluene .....	1.312	4.764	3.299	3.442	3.334	1.1
	<i>m</i> -Xylene ...	1.339	1.708				
4	Cineole .....	2.59	4.107	1.881	2.047	1.930	2.7
	<i>d</i> -Pinene ...	2.21	1.063				
	Phellandrene	0.87	0.944				
5	Cineole .....	2.59	1.571	1.832	1.943	1.824	-0.5
	<i>d</i> -Pinene ...	2.21	2.025				
	Phellandrene	0.87	1.790				

*Nitrobenzene as Solvent.*

Nitrobenzene is similar as a solvent to benzene in that the value of *b* for solutes in nitrobenzene was positive in all cases experi-

mented on. The molecular weight ( $m'$ ) of single solutes dissolved in nitrobenzene, if calculated according to equation (5), rises with increasing concentration. The results for the individual solutes are omitted here, but the results for several solutes dissolved together in nitrobenzene are given in table XIV.

As in the case of benzene, the sum of the individual depressions is always greater than the depressions obtained for the solutes when dissolved together.

The corrected calculated value ( $\Delta_2$ ), using the  $b$  correction as per equation (9), is, however, as with benzene, much nearer to the observed value.

TABLE XIV.

*Freezing-point Determinations with more than One Solute in a Common Solvent. Solvent, Nitrobenzene ( $K=7.0$ ).*

No.	Solute.	Value of "b" for solute.	Percentage weight of each solute.	$\Delta$ .	$\Delta_1$ .	$\Delta_2$ .	Percentage difference between $\Delta$ and $\Delta_2$ .
1	Toluene.....	2.295	0.926	2.439	2.534	2.463	+1
	Benzene ...	2.36	2.048				
2	Toluene ...	2.295	1.624	4.070	4.314	4.117	+1.1
	Benzene ...	2.36	3.587				
3	Toluene.....	2.295	2.401	2.800	2.929	2.820	+0.7
	<i>m</i> -Xylene ...	1.138	0.861				
	Benzene ...	2.36	0.591				
4	Toluene.....	2.295	3.919	4.323	4.671	4.399	+1.7
	<i>m</i> -Xylene ...	1.138	1.404				
	Benzene ...	2.36	0.964				
5	Toluene.....	2.295	2.574	3.599	3.883	3.672	+2.0
	<i>m</i> -Xylene ...	1.138	0.578				
	Benzene ...	2.36	1.750				

#### *Water as Solvent.*

In this case, it was not thought necessary to carry out any experimental work, as sufficient material for calculation may be obtained in the literature dealing with freezing points.

Using Abegg's numbers (*loc. cit.*), it is found that  $b$  is sometimes negative for solutes in aqueous solutions.

The values for  $b$  have been calculated for a number of solutes, and the results in table XV give the observed and calculated values for mixtures of these solutes.



TABLE XV.

*Freezing-point Determinations with more than One Solute in a Common Solvent. Solvent, Water.*

No.	Solute.	Value of "b" for solute.	Percentage weight of solute.	$\Delta$ .	$\Delta_1$ .	$\Delta_2$ .	Percentage difference between $\Delta$ and $\Delta_2$ .
1	Glycerol ...	-0.284	5.235	2.145	2.057	2.119	-1.3
	Sucrose ...	-0.24	16.857				
2	Glycerol ...	-0.284	10.90	3.48	3.294	3.431	-1.4
	Sucrose ...	-0.24	17.54				
3	Alcohol ...	-0.463	3.924	3.47	3.320	3.395	-2.1
	Glycerol ...	-0.284	8.64				
4	Alcohol ...	-0.463	5.474	4.13	4.058	4.074	-1.4
	Acetone.....	0.235	6.251				
5	Alcohol ...	-0.463	5.934	6.55	6.393	6.437	-1.7
	Acetone.....	0.235	13.555				

It will be noticed that for the solutes and solvents considered, and in spite of the corrected method of calculation employed when several solutes are used together, an error of as much as 2 per cent. occurs in some cases. This error is sometimes positive and sometimes negative, and may be due, (i) to reaction between the various solutes, or (ii) to action of the solute on the solvent, or (iii) to experimental errors in determining the freezing point of the solutions.

When freezing-point determinations are to be used for purposes of analysis, these errors have to be taken into account. Before the method can be applied directly to a given sample, the errors of determination must have been ascertained by experiments on somewhat similar material.

#### *Summary.*

(1) In freezing-point determinations, there may with advantage be substituted for  $W$ , the weight of solvent, the expression  $W + bw$ , where  $w$  is the weight of the solute and  $b$  is a constant which depends both on the solute and the solvent, and is at present determinable only by experiment with the solute and solvent.

(2) When several solutes are dissolved at one time in the same solvent, then, if  $b$  is positive for the individual solutes, the sum of the individual depressions of the freezing point by the various solutes is greater than the observed depression of the freezing point; if  $b$  is negative for each individual solute, the sum of the

individual depressions is less than the observed depression of the freezing point.

(3) If several solutes are dissolved together in a solvent and the quantity of solvent be taken as  $W + w_1b_1 + w_2b_2 + w_3b_3 +$ , where  $W$  is the actual weight of the solvent, and  $w_1, w_2, w_3$  are the weights of the solutes, and  $b_1, b_2, b_3$  are the values of the constant  $b$  for each solute, as explained in paragraph (1) above, then the sum of the calculated values of the depressions of the individual solutes differs from the observed total depressions by only a small error in all cases considered by the author.

I desire to thank Mr. C. H. Fischer for carrying out the experimental work described in this paper.

CHEMICAL DEPARTMENT,  
UNIVERSITY OF SYDNEY.

[Received, April 14th, 1919.]

## LXII.—The Use of Freezing-point Determinations in Quantitative Analysis.

By CHARLES EDWARD FAWSITT.

CONSIDERABLE use has been made of freezing-point determinations as an aid to analytical work in recent years.

The freezing point of a liquid like milk or blood serum has been used as a characteristic for these substances independently of what the constituent solutes are.

Fox and Barker (*J. Soc. Chem. Ind.*, 1917, **36**, 842) have made use of a determination of the freezing point to obtain the percentage of phenol in commercial cresylic acid. There is a little uncertainty in using the freezing-point results in such a case, because the other substances in crude cresylic acid, namely, the three cresols, have all the same molecular weight.

Weiss and Downs (*ibid.*, 863) show that the percentage of phenol in tar oils may be determined by a freezing-point determination provided a density determination of the mixture is also carried out.

Drapier (*Compt. rend.*, 1915, **161**, 461) has suggested that the percentage of one ingredient  $A_1$  in a mixture  $A$  could be obtained provided that one knows the lowering of the freezing point by the mixture  $A$  (solute) when dissolved in  $A_1$  (solvent), and also when  $A$  is dissolved in some other solvent,  $S$ , which is not an ingredient of  $A$ . Drapier, however, has apparently not followed up this

TABLE XV.

*Freezing-point Determinations with more than One Solute in a Common Solvent. Solvent, Water.*

No.	Solute.	Value of "b" for solute.	Percentage weight of solute.	$\Delta$ .	$\Delta_1$ .	$\Delta_2$ .	Percentage difference between $\Delta$ and $\Delta_2$ .
1	Glycerol ...	-0.284	5.235	2.145	2.057	2.119	-1.3
	Sucrose ...	-0.24	16.857				
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It will be noticed that for the solutes and solvents considered, and in spite of the corrected method of calculation employed when several solutes are used together, an error of as much as 2 per cent. occurs in some cases. This error is sometimes positive and sometimes negative, and may be due, (i) to reaction between the various solutes, or (ii) to action of the solute on the solvent, or (iii) to experimental errors in determining the freezing point of the solutions.

When freezing-point determinations are to be used for purposes of analysis, these errors have to be taken into account. Before the method can be applied directly to a given sample, the errors of determination must have been ascertained by experiments on somewhat similar material.

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suggestion by publishing any experimental support for the method. It seemed to the author, however, that this method was worth while investigating.

*Theoretical.*—Let us suppose that the depression of freezing point produced by dissolving a solute in a solvent is (1) proportional to the concentration of the solute, (2) inversely proportional to the molecular weight of the solute if equal weights of different solutes are compared; let us suppose, further, (3) that a solute exercises its usual effect in depressing the freezing point of a solvent independently of the presence or absence of other solutes.

Conditions (1) and (2) are approximately true for most dilute solutions. The effect of one solute on the depression of the freezing point of a solvent, when another second solute is present (3), has not yet been very thoroughly investigated, but in several investigated cases (3) certainly does not hold quite true even in dilute solution (see preceding paper). In developing the theory of this process it will, however, be assumed in the first instance that (1), (2), and (3) hold good. Consider a liquid mixture  $A$ . The mixture  $A$  is made up of several ingredients,  $A_1, A_2, A_3, A_4$ , etc. . . .  $A_n$ . It is required to find out the percentage of the ingredient  $A_1$ . The ingredient  $A_1$  must be such that it is capable of being frozen at a convenient temperature.

Obtain also a solvent,  $S$ , in which  $A$  is completely soluble;  $S$  must also be a substance (liquid) which can be frozen at a convenient temperature.

A small quantity,  $a$ , of the substance  $A$  is dissolved in  $P$  grams of the solvent  $S$ , and the depression in the freezing point of  $S$  noted. Call this  $\Delta_s$ . Also a quantity of the mixture  $A$ , say  $b$  grams, is dissolved in  $Q$  grams of the solvent  $A_1$ , and the depression in the freezing point of  $A_1 = \Delta_{A_1}$  noted.

Further, let  $a = a_1 + a_2 + a_3 + a_4 \dots$ , where  $a_1, a_2$ , etc., are the weights of the several ingredients  $A_1, A_2$ , etc., in  $a$ ; let  $b = b_1 + b_2 + b_3 + b_4 \dots$ , where  $b_1, b_2$ , etc., are the weights of the ingredients  $A_1, A_2$ , etc., in  $b$ ; let  $K_1$  = the cryoscopic constant for the solvent,  $S$ , that is, the depression produced in the freezing point of  $S$  by dissolving in 1000 grams of  $S$  one gram-molecular weight of any solute; let  $K_2$  = the cryoscopic constant for the solvent  $A_1$ ; let  $m_1, m_2, m_3 \dots$  be the molecular weights of the constituents  $A_1, A_2, A_3 \dots$ , then

$$\Delta_s = \frac{1000 K_1}{P} \left( \frac{a_1}{m_1} + \frac{a_2}{m_2} + \frac{a_3}{m_3} + \dots \right) \quad (1)$$

and

$$\Delta_{A_1} = \frac{1000 K_2}{Q + b_1} \left( \frac{b_2}{m_2} + \frac{b_3}{m_3} + \dots \right) \quad (2)$$

Now if  $a/b=r$ , (2) becomes

$$\Delta_{A_1} = \frac{1000 K_2}{(Q+b_1)r} \cdot \left( \frac{a_2}{m_2} + \frac{a_3}{m_3} + \dots \right) \dots \quad (3)$$

Multiplying equation (1) by  $\frac{K_2}{(Q+b_1)r}$ , and (3) by  $\frac{K_1}{P}$ , we get

$$\frac{K_2 \Delta_s}{(Q+b_1)r} - \frac{K_1 \Delta_{A_1}}{P} = \frac{K_1 K_2 \times 1000}{P \cdot (Q+b_1) \cdot r} \cdot \frac{a_1}{m_1}$$

$$\therefore a_1 = \frac{m_1 (K_2 \Delta_s P - K_1 \Delta_{A_1} r Q)}{K_1 (1000 K_2 + m_1 \Delta_{A_1})} \dots \quad (4)$$

It has, however, been pointed out (see preceding paper) that in dealing with ordinary concentrations, the weights of solvent should not be taken as  $P$  and  $(Q+b_1)$ , but that these values should be corrected by the addition of a term depending on the weight of solute present.  $P$  would then become

$$P + \delta_1 a_1 + \delta_2 a_2 + \delta_3 a_3 + \delta_4 a_4 + \dots,$$

where  $\delta_1, \delta_2, \delta_3 \dots$  are constants for each ingredient of the solute  $= P + \delta a$ , where  $\delta$  is the average value of the constants  $\delta_1, \delta_2, \delta_3, \delta_4$  for the several ingredients of the solute  $A$ . Similarly,  $Q+b_1$  would become  $Q+b_1 + \gamma(b_2 + b_3 + b_4 + \dots)$ , where  $\gamma$  is the average value of the correction factor for the solutes  $A_2, A_3, A_4, A_5$ , etc.

Formula (4) then becomes

$$a_1 = \frac{m_1 [K_2 \Delta_s (P + \delta a) - K_1 \Delta_{A_1} \{Q + \gamma(b_2 + b_3 + b_4 + \dots)\} r]}{K_1 (1000 K_2 + m_1 \Delta_{A_1})} \dots \quad (5)$$

It may be wondered how the value for  $b_1$  can be obtained for insertion in this formula (5). To obtain this, a calculation of  $a_1$  is first made, using formula (4). Then  $b_1 = a_1/r$ . This value, which is only roughly, but yet sufficiently, accurate is used for a more accurate determination of  $a_1$ , according to equation (5).

The values of  $\delta$  and  $\gamma$  can be obtained directly from the experiment used in determining  $a_1$ .

In many cases it will be necessary to introduce a further correction in the formula. It has already been pointed out in the preceding paper that the depression of freezing points caused by a number of solutes in one solvent is somewhat different from the expected value even after due allowance has been made by the correction in the amount of solvent as used in obtaining equation (5) from equation (4).

The values of  $\Delta_s$  and  $\Delta_{A_1}$  should, then, be corrected further by an amount which can only be determined by previous experiment on the class of solute which is under investigation.

Let us use the correction factors (constants)  $U$  and  $V$  for  $\Delta_s$  and  $\Delta_{A_1}$ .

The percentage of  $A_1$  in  $A$  is then

$$\frac{100 \cdot m_1 [K_2 \Delta_s U(P + \delta a) - K_1 \Delta_{A_1} \{Q + \gamma(b - b_1)\} r \cdot V]}{a \cdot K_1 [1000 K_2 + \Delta_{A_1} m_1]} \quad (6)$$

Another correction which must sometimes be introduced is due to the fact that when  $A_1$  is dissolved in the solvent  $S$ , the calculated molecular weight may not be exactly  $m_1$ , but some other value, say  $m'_1$ . This value, if appreciably different from  $m_1$ , should be substituted for  $m_1$ . The formula to be used is then: percentage of

$$A_1 = \frac{100 \cdot m_1' [K_2 \Delta_s U(P + \delta a) - K_1 \Delta_{A_1} \{Q + \gamma(b - b_1)\} r \cdot V]}{a K_1 [1000 K_2 + \Delta_{A_1} m_1']} \quad (7)$$

In considering what estimations the method might usefully be applied to, the author thought that the determination of (a) benzene in light coal-tar oils was a suitable case, also (b) the determination of cineole in eucalyptus oils. With regard to (a), the determination of benzene can be obtained approximately (1) by distillation, (2) sometimes by direct determination of the freezing point, especially after addition of extra benzene, (3) by nitration, with subsequent determination of the products, but the method at present under discussion would sometimes be found more suitable.

With regard to the determination of cineole in eucalyptus oils, the phosphoric acid method, although fairly satisfactory as a rule, requires a comparatively large quantity of oil (10 grams). The resorcinol method has been used a good deal lately by H. G. Smith, but he has informed the author that in certain cases it is not trustworthy.

In the following experiments, as ordinary "Beckmann" type of thermometer graduated to  $0.01^\circ$  was used.

#### *Estimation of Benzene in Mixtures.*

The mixtures were used as solutes in depressing the freezing point of nitrobenzene and of benzene.

$K_2$  for benzene = 5.0;  $K_1$  for nitrobenzene = 7.0.

The results were calculated according to the formula: percentage of benzene =

$$\frac{100 \times 78 [5 \cdot \Delta_s \cdot (P + 2.3a) \cdot 1.018 - 7 \cdot \Delta_{A_1} \cdot \{Q + 1.4(b - b_1)\} \cdot 1.008 \cdot r]}{a \cdot 7 \cdot [5000 + \Delta_{A_1} \cdot 78]}$$

*Mixture A.*

The composition of the mixture was: benzene 68.85, toluene 31.15 per cent.

TABLE I.

*Freezing-point Determinations  
in Nitrobenzene as Solvent.*

No.	Percentage of solute.	$\Delta_{\text{f.}}$
1	1.010	0.86
2	2.159	1.819
3	2.974	2.439
4	4.070	3.266
5	5.211	4.07

TABLE II.

*Solvent, Benzene.*

No.	Percentage of solute.	$\Delta_{\text{f.}}$
1	1.580	0.30
2	3.941	0.702
3	6.541	1.130
4	9.22	1.550
5	11.88	1.920

TABLE III.

*Calculation of Percentage of Benzene in Mixture A.*

Observations used.		Percentage calculated.
Table I. No. 1	Table II. No. 2	
3	3	69.6
5	3	70.2
	5	70.4

*Mixture B.*

The composition of the mixture was: benzene 15.3, toluene 62.4, *m*-xylene 22.3 per cent.

TABLE IV.

*Solvent, Nitrobenzene.*

No.	Percentage of solute.	$\Delta_{\text{f.}}$
1	1.383	1.040
2	2.589	1.909
3	3.853	2.800
4	5.273	3.691
5	6.287	4.323

TABLE V.

*Solvent, Benzene.*

No.	Percentage.	$\Delta_{\text{f.}}$
1	1.392	0.642
2	3.131	1.438
3	4.844	2.169
4	6.409	2.789
5	7.734	3.299

TABLE VI.

*Calculation of Percentage of Benzene in Mixture B.*

Observations used.		Percentage calculated.
Table IV. No. 1	Table V. No. 1	
2	2	14.1
3	2	13.4
3	3	14.9
4	4	15.0



*Mixture C.*

The composition of the mixture was: benzene 10.00, toluene 61.48, *m*-xylene 9.19, *o*-xylene 8.56, *p*-xylene 9.06, thiophen 1.71 per cent.

TABLE VII.

*Solvent, Nitrobenzene.*

No.	Percentage of solute.	$\Delta_s$ .
1	1.193	0.898
2	2.302	1.684
3	3.627	2.577

TABLE VIII.

No.	Percentage of solute.	$\Delta_{A_1}$ .
1	1.488	0.737
2	2.925	1.417
3	4.248	1.980

TABLE IX.

*Calculation of Percentage of Benzene in Mixture C.*

Observations used.		Percentages calculated.
Table VII.	Table VIII.	
1	1	8.3
3	3	10.2

*Estimation of Cineole in Mixtures.*

The mixtures were made of cineole, pinene, and *l*- $\alpha$ -phellandrene. The mixtures were used as solutes in depressing the freezing points of benzene and of cineole.

$K_1$  for benzene = 5.0;  $K_2$  for cineole = 6.7.

The results were calculated according to the formula: percentage of cineole =

$$\frac{100 \times 146[6.7 \cdot 1.02 \cdot \Delta_s \cdot (100 + 1.7a) - 5.0 \times 1.04 \cdot \Delta_{A_1} \cdot \{100 + 1.7(b - b_1)r\}]}{a \cdot 5[6700 + \Delta_{A_1} \cdot 146]}$$

It will be noticed that 146 (obtained by experiment) was used for the molecular weight of cineole in benzene, instead of 154, the theoretical value.

*Mixture D.*

The composition of the mixture was: cineole 67.1, pinene 17.5, phellandrene 15.4 per cent.

TABLE X.

*Solvent, Benzene.*

No.	Percentage of solute.	$\Delta_s$ .
1	1.887	0.642
2	3.948	1.313
3	5.759	1.881

TABLE XI.

*Solvent, Cineole.*

No.	Percentage of solute.	$\Delta_{A_1}$ .
1	3.59	0.568
2	8.20	1.262
3	13.72	2.051

TABLE XII.

*Calculation of Percentage of Cineole in Mixture D.*

Observations used.		Percentage calculated.
Table X.	Table XI.	
1	1	67.2
2	2	68.5
3	3	67.8

*Mixture E.*

The composition of the mixture was: cineole 29.2, pinene 37.6, phellandrene 33.2 per cent.

TABLE XIII.

*Solvent, Benzene.*

No.	Percentage of solute.	$\Delta_d$ .
1	1.786	0.633
2	3.57	1.244
3	5.39	1.832

TABLE XIV.

*Solvent, Cineole.*

No.	Percentage of solute.	$\Delta_{d_1}$ .
1	1.48	0.518
2	3.957	1.356
3	6.63	2.210

TABLE XV.

*Calculation of Percentage of Cineole.*

Observations used.		Percentage calculated.
Table XIII.	Table XIV.	
1	1	28.4
2	2	28.1
3	3	29.4

*Mixture F.*

The composition of the mixture was: cineole 54.3, pinene 24.3, phellandrene 21.4 per cent.

TABLE XVI.

*Solvent, Benzene.*

No.	Percentage of solute.	$\Delta_d$ .
1	1.708	0.599
2	3.596	1.219

TABLE XVII.

*Solvent, Cineole.*

No.	Percentage of solute.	$\Delta_{d_1}$ .
1	2.124	0.479
2	7.580	1.655

TABLE XVIII.

*Calculation of Percentage of Cineole in Mixture F.*

Observations used.		Percentage calculated.
Table XVI.	Table XVII	
1	1	55.0
2	2	52.9

From these results, it will be seen that the calculation yields figures which are within about 2 units of the true percentage. This error is completely accounted for by errors of experiment, more particularly the reading of the thermometer. It is not possible to be sure that the calculated percentage is any nearer to the true result than this, using the Beckmann freezing-point apparatus in the ordinary way. As unknown mixtures might in some cases contain unknown ingredients, it would be impossible, unless with previous experience with similar mixtures, to know the values of  $U$  and  $V$  in equation (7), and any tentative value used for  $U$  or  $V$  might result in a rather large error in the calculated percentage. In certain cases of this kind experimented on, the error in the percentage was as high as 8 units. The error is stated above as so many units, because in the formula (7), for the calculation of the percentage of  $A_1$ , one term containing  $\Delta_{A_1}$  is subtracted from another containing  $\Delta_1$ , giving a number which varies directly as the final result (percentage of  $A_1$ ). It is not therefore possible to express the error of experiment as a percentage.

#### *Summary.*

The method of estimating an ingredient  $A_1$  in a substance  $A$  by finding the freezing-point depression of  $A$  in  $A_1$  (as solvent), and also in some other solvent,  $S$ , may be applied in special cases where it is possible to experiment previously with samples of substance somewhat similar to  $A$ . The percentage of  $A_1$  can then be determined in certain cases to an accuracy of about two units with the ordinary freezing-point apparatus.

When it is not possible to experiment with the same class of substance beforehand, the method of determination is liable to give a result with a much larger error. The method can therefore only be recommended when (1) there has been previous experience with the same class of substance, or (2) when other possible methods of determination are not capable of a greater degree of accuracy, or (3) where other methods require for their successful application a larger quantity of substance than is available. The freezing-point method already described requires for its successful application about 1 gram of substance, but it is more satisfactory if a larger amount, say 4—6 grams, is available.

I wish to thank Mr. C. H. Fischer for carrying out the experimental work in this paper.

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[Received, April 14th, 1919.]

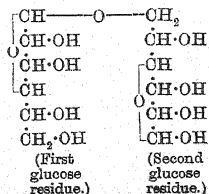
LXIII.—*The Constitution of the Disaccharides.*  
*Part III. Maltose.*

By WALTER NORMAN HAWORTH and GRACE CUMMING LEITCH.

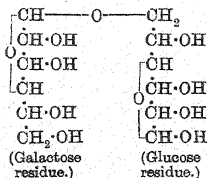
MALTOSE is a reducing sugar which yields, on hydrolysis with dilute acid or with the enzyme maltase, two molecular proportions of glucose. Consequently, it is regarded as a biose having the reducing group of one glucose molecule united through an anhydride linking with a second glucose residue. Confirmation of this view is found in the oxidation of maltose to maltobionic acid, which gives rise on hydrolysis to glucose and gluconic acid (Fischer and Meyer, *Ber.*, 1889, 22, 1941).

No evidence has hitherto been available indicating which of the hydroxyl groups of the second glucose residue is involved in this union (see formula I). The present authors have shown in Part II of this series of communications (T., 1918, 113, 188) that in lactose the reducing group of the galactose residue is linked with the hydroxyl group of the penultimate carbon atom of the glucose molecule. The possibility that this mode of linking was present also in maltose appeared improbable in view of Hudson's observation (*J. Amer. Chem. Soc.*, 1916, 38, 1566) that lactose exhibits a close parallelism with cellobiose and not with melibiose, to which a different constitution has been assigned (Haworth and Leitch, *loc. cit.*). There was, however, no definite ground for excluding this possibility in the case of maltose, nor, indeed, for assuming that any one hydroxyl group attached to the third, fifth, or sixth carbon atom from the reducing end of the second glucose chain could not equally well be concerned in the union of the two molecules of the hexose.

In the course of the present investigation, this uncertainty has been removed, and it has been shown that maltose must have the constitution indicated below, and thus corresponds structurally,



(I) Maltose.



Melibiose.

among the diglucose disaccharides, with melibiose of the glucose-galactose class.

This constitution assigned to maltose is identical with the current provisional formula which has found expression in recent text-books, and was proposed, along with alternative formulæ, by Fischer ("Untersuchungen über Kohlenhydrate und Fermente," 1884—1908, p. 92).

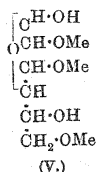
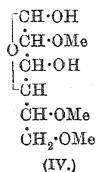
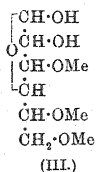
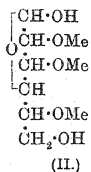
Following the general lines indicated in the previous research on lactose (*loc. cit.*), the methylation of maltose was effected by the agency of methyl sulphate and sodium hydroxide, and, as a precautionary measure designed to ensure that methylation was complete, the material isolated from this reaction was finally submitted to an alternative treatment with Purdie's reagent, namely, silver oxide and methyl iodide. Eight methyl groups were found to have been introduced into the maltose molecule, and heptamethyl methylmaltoside (VII), corresponding in the degree of substitution with the known octa-acetylmaltose, was isolated as a colourless gum, which distilled as a mobile syrup at 189—190°/0.09 mm. The compound was soluble in water and did not reduce Fehling's solution. It dissolved freely in methyl or ethyl alcohol or acetone, and showed  $[\alpha]_D + 89.6^\circ$ , the equilibrium value for maltose itself being 137.7°.

There can be little doubt, in view of other results obtained in methylating reducing sugars with methyl sulphate, that this substance is chiefly the  $\beta$ -form, containing also the stereochemical  $\alpha$ -modification.

When heptamethyl methylmaltoside was hydrolysed with 5 per cent. aqueous hydrochloric acid for three hours at 85—100°, a mixture of tetramethyl and trimethyl glucoses was obtained as the product of cleavage. This was a mobile syrup, and the separation of the two constituents was effected by careful fractionation in the high vacuum of the Gaede pump. Two pure fractions, collected at 131°/0.3 mm. and at 171°/0.23 mm., were isolated along with the transition fraction distilling at temperatures intermediate between these limits. From the transition fraction, as will be shown later, more of the pure fractions was isolated. The first fraction, distilling at the lower temperature, crystallised immediately on nucleation with a crystal of tetramethyl glucose (VIII), and its complete identity with the latter substance was proved by determination of the melting point and also of that of a mixture with an authentic specimen of tetramethyl glucose. The specific rotation of the specimen derived from the hydrolysis of the methylated methylmaltoside was in agreement with the accepted

equilibrium value, which is  $[\alpha]_D + 83^\circ$ . We can therefore confirm the similar observation made by Purdie and Irvine (T., 1905, **87**, 1029), who also isolated this compound from the product obtained by methylating maltose with silver oxide and methyl iodide.

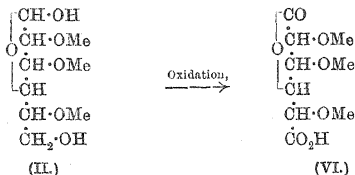
The identification of the substance distilling at  $171^\circ/0.23$  mm. presented greater difficulty. The analytical results were in agreement with the formula of a trimethyl glucose. It reduced Fehling's solution, and its comparative stability towards permanganate indicated that it was a reducing sugar of the butylene oxide type. It did not crystallise after nucleation with a specimen of the trimethyl glucose isolated from the hydrolysis of heptamethyl methyl-lactoside (Haworth and Leitch, *loc. cit.*), and failed to give an osazone with phenylhydrazine. Of the four formulæ possible for a trimethyl glucose of the butylene oxide type, those numbered III and V may for these reasons be excluded from immediate consideration.



Moreover, it is clear from the presentation of these four possible formulæ that if proof could be found for the presence of a free primary alcohol group in the trimethyl glucose isolated during this investigation, this fact would definitely determine the constitution of the trimethyl hexose, as this terminal hydroxyl group is only present in formula II.

Accordingly, the trimethyl glucose was carefully oxidised with dilute nitric acid (D 1.2), and a liquid carboxylic acid was isolated which was shown also to be a lactone. On titration with *N*/10-alkali, an apparent neutral point was reached when rather less than one molecular proportion of alkali was introduced, and its behaviour on the subsequent addition of more alkali showed that a lactone ring was undergoing scission. Two molecular proportions of alkali were needed for complete neutralisation. The analytical data indicated that the lactonic acid had the molecular formula  $\text{C}_6\text{H}_4\text{O}_7$ , and contained three methoxyl groups. Its constitution can therefore only be represented by formula VI, and consequently the formula of the trimethyl glucose, from which by

oxidation the lactonic acid was obtained, is represented by formula II.

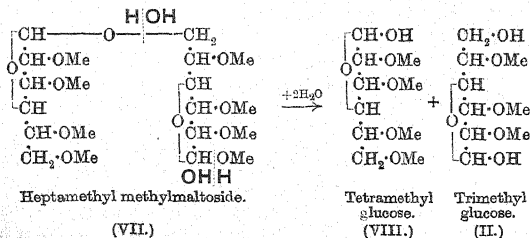


The product of oxidation is thus trimethyl saccharo-monolactone, and the primary alcohol group is shown to be present in the trimethyl glucose, since only such a group could undergo oxidation to a carboxyl group. This primary alcohol group has become exposed during the dissolution of partnership with the second methylated glucose residue occasioned by the hydrolysis of the biose.

The change in rotatory power, characteristic of lactones of the sugar series, was observed in the case of the lactonic acid. In aqueous solution, the value decreased from  $[\alpha]_D +78^\circ$  to  $+40^\circ$  during four hours. In contact with a trace of hydrochloric acid, the value increased again to  $+56^\circ$ .

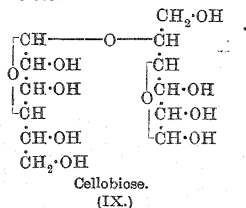
A molecular weight determination in acetone solution by the ebullioscopic method gave the number 242, which is in fairly close agreement with that required (234) for the molecular formula  $\text{C}_{19}\text{H}_{34}\text{O}_{17}$ .

The behaviour of heptamethyl methylmaltoside (VII) on hydrolysis must therefore be formulated by the scheme outlined below, the dotted lines indicating the points of cleavage:



Inasmuch as ordinary crystalline maltose is hydrolysed by contact with the enzyme maltase and not by emulsin, the disaccharide is to be regarded as glucose- $\alpha$ -glucoside, and since it exhibits an

upward mutarotation and belongs to the *d*-series, it may be described stereochemically as  $\beta$ -glucose- $\alpha$ -glucoside, and is structurally represented by formula I (p. 809). *iso*Maltose has probably the same structure, but is a glucose- $\beta$ -glucoside. Maltose resembles melibiose in its behaviour (Bau, *Chem. Zeit.*, 1897, 21, 186), and so also cellobiose has properties in common with lactose (Hudson, *loc. cit.*). Definite structural formulæ have been assigned to one member in each of these pairs of disaccharides, namely, lactose and maltose, and it is legitimate, therefore, to assign a provisional structural formula to cellobiose (IX), especially in view of the fact that Denham and Woodhouse isolated from methylated cellulose on hydrolysis the same crystalline trimethyl glucose as the present authors obtained from methylated lactose (T., 1917, 111, 244; 1918, 113, 188). This cellobiose formula is of the same structural type as lactose:



Experiments are at present in progress to confirm this provisional constitution.

#### EXPERIMENTAL.

##### *Methylation of Maltose with Methyl Sulphate: Preparation of Heptamethyl Methylmaltoside.*

Maltose (30 grams) prepared by the action of barley diastase on potato starch was dissolved in the minimum volume of warm water. To the cooled solution methyl sulphate (28.5 c.c.) was added, and a 30 per cent. solution of sodium hydroxide (29 c.c.) was introduced very gradually with stirring. During the addition of the latter, the temperature was maintained at 35–40°, and the mixture kept overnight. The reducing action of the maltose towards Fehling's solution had then completely disappeared, and methylmaltoside had obviously been formed. The methylation of the remaining hydroxyl groups was effected at 70°, and the solution maintained faintly alkaline throughout. Methyl sulphate (85.5 c.c.) was added slowly at this temperature with efficient



mechanical stirring, and simultaneously 30 per cent. sodium hydroxide (82 c.c.) was introduced. It is important that the reagents should be added very gradually; a separate dropping funnel was kept for each reagent. The second part of the methylation, which has just been described, occupied one and a-half hours, after which the temperature was raised to  $100^{\circ}$  for half an hour. Extraction of the methylated maltoside with chloroform yielded, after drying over anhydrous magnesium sulphate and distillation of the solvent, 39 grams of a crude, straw-yellow syrup. This was subjected to another similar methylation at  $70^{\circ}$  with methyl sulphate, and, after careful removal of the whole of the chloroform used for the extraction, the residue weighed 28.2 grams.

By distillation in the high vacuum of the Gaede pump, 23 grams of a colourless syrup were collected at about  $195^{\circ}/0.28$  mm. In order to ensure complete methylation of all the hydroxyl groups, this product was again methylated with alternative reagents, namely, with silver oxide and methyl iodide. The material was isolated in the usual way after this treatment, and yielded a colourless syrup distilling at  $187^{\circ}/0.06$  mm. All the still residues were again methylated, and provided a further quantity of the required product. At this stage, the material from several preparations was combined and redistilled, when almost the whole distilled at  $189\text{--}190^{\circ}/0.09$  mm., and showed  $n_D$  1.4698. The compound was devoid of any reducing action on Fehling's solution, and behaved as a glucoside.

A methoxyl estimation indicated that complete methylation had taken place, eight methoxyl groups having been inserted in the maltose residue:

0.1290 gave 0.2493  $\text{CO}_2$  and 0.0957  $\text{H}_2\text{O}$ .  $\text{C}=52.7$ ;  $\text{H}=8.24$ .

0.0995 „ 0.4034  $\text{AgI}$ .  $\text{OMe}=53.52$ .

$\text{C}_{12}\text{H}_{14}\text{O}_8(\text{OMe})_8$  requires  $\text{C}=52.86$ ;  $\text{H}=8.37$ ;  $\text{OMe}=54.63$  per cent.

The specific rotation of the heptamethyl methylmaltoside was determined in various solvents as follows:

Solvent.	$c$ .	$\alpha_D$ .
Methyl alcohol .....	1.313	+89.5°
Ethyl alcohol .....	1.395	+89.6°
Acetone .....	1.173	+89.5°
Water .....	1.345	+81.4°

As the specific rotation in water appears slightly lower than was expected, an opportunity will be taken to confirm this value.

*Hydrolysis of Heptamethyl Methylmaltoside.*

Preliminary experiments indicated that the hydrolysis could best be effected with 5 per cent. aqueous hydrochloric acid solution at 85—100°. These conditions were also observed with the main bulk of the material, weighing 30 grams, which was dissolved in 400 c.c. of dilute acid of the above concentration. The solution was heated for one and a-half hours at 85°, and for a similar period at 100°. The mixture showed an initial rotation of  $\alpha +12.9^\circ$ , and the final reading was  $9.8^\circ$ . Further heating of a small sample of the solution produced no change in the rotation value. The procedure for the isolation of the products consisted in neutralisation with excess of barium carbonate, followed by filtration and evaporation of the filtrate under diminished pressure, when a syrup contaminated with barium chloride was obtained. The mineral matter was removed by extraction of the syrup with alcohol. After removal of this solvent, the residue was extracted with ether and the ethereal solution distilled. The syrup isolated in this way weighed 25 grams, and was carefully fractionated in a high vacuum.

- Fraction I.—B. p. 120—131°/0.3 mm. Weight, 8.2 grams.  
 „ II.—B. p. 131—155°/0.23 mm. Weight, 8.4 grams.  
 „ III.—B. p. 171°/0.23 mm. Weight, 5.4 grams.

The first of these fractions crystallised immediately on nucleation with a specimen of tetramethyl glucose of the butylene oxide form. Fraction II was obviously a transition fraction which partly crystallised, and from it further quantities of the first and third fractions were ultimately obtained by repeated distillation. Fraction III had a boiling point which corresponded with that of a trimethyl hexose. All the fractions were colourless syrups which failed to give osazones and were not easily oxidised with permanganate. A recrystallisation of fraction I produced the easily recognisable needles of tetramethyl glucose, and its identity with this compound was shown by the rotatory power (see Purdie and Irvine, T., 1904, **85**, 1049), which was  $[\alpha]_D +83^\circ$  (equilibrium value) in water. Moreover, the melting point was correct for this substance, and a mixed melting-point determination showed no depression. The isolation of this substance from methylated maltose confirms the earlier observation recorded by Purdie and Irvine (T., 1905, **87**, 1029).

An analysis of fraction III, which showed  $n_D 1.4792$ , gave the following results:

0.1394 gave 0.2480  $\text{CO}_2$  and 0.1060  $\text{H}_2\text{O}$ .  $\text{C}=48.52$ ;  $\text{H}=8.02$ .

$\text{C}_9\text{H}_{18}\text{O}_6$  requires  $\text{C}=48.62$ ;  $\text{H}=8.11$  per cent.

An estimation of the methoxyl content characterised the substance as a trimethyl hexose:

0.1120 gave 0.3527  $\text{AgI}$ .  $\text{OMe}=41.6$ .

$\text{C}_6\text{H}_9\text{O}_3(\text{OMe})_3$  requires  $\text{OMe}=41.9$  per cent.

The specific rotatory power of the trimethyl hexose was determined as follows:

Solvent.	$c$ .	$\alpha_D$ .
Methyl alcohol.....	2.123	+67.8°
Acetone.....	2.151	+61.4°
Water .....	1.816	+69.3° $\rightarrow$ 71.0° (final value)

*Oxidation.*—With the object of determining the constitution of this hexose derivative, which clearly must represent one of the glucose residues of the maltose molecule, and therefore must be a trimethyl glucose, 3.5 grams of the substance were oxidised by gentle digestion with 40 c.c. of dilute nitric acid ( $\text{D } 1.2$ ). To initiate the reaction, the temperature was maintained at  $80^\circ$  for a few minutes, and thereafter at  $68^\circ$  for three and a-half hours. Nitrous fumes had ceased to be evolved by this time, and the solution was almost colourless. The water was evaporated under diminished pressure at  $35\text{--}40^\circ$ ; more water was repeatedly added during this procedure, and the solution again concentrated with the view of removing the whole of the nitric acid. Similar treatments with ethyl alcohol, followed by evaporation in a vacuum, served to eliminate the mineral acid, and the procedure was repeated with dry ether. Finally, a pale yellow syrup was obtained, which was dried and prepared for analysis by heating at  $90^\circ$  in a vacuum while passing through it a current of dry air. The weight of this oxidation product was 2.7 grams:

0.1094 gave 0.1847  $\text{CO}_2$  and 0.0618  $\text{H}_2\text{O}$ .  $\text{C}=46.03$ ;  $\text{H}=6.26$ .

0.0999 „ 0.2720  $\text{AgI}$ .  $\text{OMe}=35.9$ .

$\text{C}_6\text{H}_9\text{O}_4(\text{OMe})_3$  requires  $\text{C}=46.15$ ;  $\text{H}=6.0$ ;  $\text{OMe}=39.7$  per cent.

From the above figures, the substance appeared to be a trimethyl saccharolactone, and this view was confirmed by titration with alkali.

0.0995 Gram was dissolved in dilute alcohol and rapidly titrated with  $N/10$ -sodium hydroxide, using phenolphthalein as indicator. When about 4.5 c.c. of the standard alkali had been added, the colour of the indicator remained for a few minutes and then disappeared. With each subsequent addition of alkali up to the amount of 9 c.c., the same phenomenon was observed. Excess of alkali was now introduced and the solution heated for

half an hour, and finally titrated to neutral point with standard acid. The amount of *N*/10-sodium hydroxide required for the complete neutralisation was 9.8 c.c., whereas a lactonic acid of the formula  $C_9H_{14}O_7$  requires 9.7 c.c.

The specific rotation of trimethyl saccharolactone was determined in aqueous solution, and showed  $[\alpha]_D^{78^\circ}$ , falling to the value  $+40^\circ$  after four hours. On catalysis with a trace of hydrochloric acid, the value again increased to  $+56^\circ$ . A molecular weight determination in acetone solution by the ebullioscopic method gave the number 242, whilst the molecular weight required by the formula of the lactonic acid,  $C_9H_{14}O_7$ , is 234.

The authors are grateful to the Carnegie Trust for the grant of a Research Fellowship to one of them.

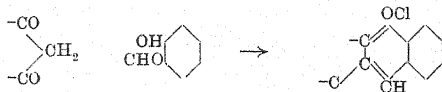
UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,  
UNIVERSITY OF ST. ANDREWS.

[Received, June 2nd, 1919.]

## LXIV.—Condensation of Deoxybenzoin and Aldehydes.

By ANANDA KISORE DAS and BROJENDRA NATH GHOSH.

It has been shown that aromatic *o*-hydroxy-aldehydes condense with substances containing  $\cdot CO \cdot CH_2 \cdot CO \cdot$  groups as in 1:3-diketohydrindene (Sastry and Ghosh, T., 1915, 107, 1442), and in acetyl or benzoyl acetone (Chatterjee and Ghosh, T., 1918, 113, 444) to form pyranol derivatives of the type



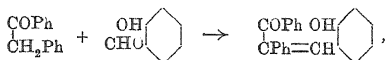
In order to extend this investigation, a substance of a similar type, namely, deoxybenzoin, was employed. In this case, instead of a  $\cdot CO \cdot CH_2 \cdot CO \cdot$  group, a  $\cdot CH_2 \cdot$  group is situated between one  $\cdot CO \cdot$  group and the other phenyl group.

Several investigators have studied the interaction of benzaldehyde and deoxybenzoin, both acid and alkali being used as condensing agents (Japp and Klingemann, *Ber.*, 1888, 21, 2935; Knoevenagel and Weissgerber, *Ber.*, 1893, 26, 337; Stobbe and Niedenzu, *Ber.*, 1901, 34, 3897; Klages and Tetzner, *Ber.*, 1902, 35, 3971).

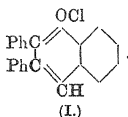
As our object was to synthesise pyranol derivatives, we began

H H\*

with the condensation of salicylaldehyde and deoxybenzoin. It appeared that in the presence of alkali hydroxides, the condensation might proceed in the following way:



giving salicylidenedeoxybenzoin, which in the presence of hydrogen chloride might yield 2:3-diphenylbenzopyryonium chloride (I).



Accordingly, we conducted the reaction in the presence of alkali hydroxide, but found that no condensation took place under the conditions of the experiment. With hydrogen chloride, however, we obtained the desired compound. Decker and von Fellenberg (*Annalen*, 1909, **364**, 31) obtained the corresponding ferrichloride.

It was also found that no interaction took place between *p*-hydroxybenzaldehyde and deoxybenzoin in the presence of alkali hydroxide, but with hydrogen chloride the condensation product was formed; it could not, however, be obtained in a pure state.

Failing to obtain condensation products in the above two cases with alkali hydroxide, we extended the experiment to other aldehydes, such as anisaldehyde, piperonal, and *p*-tolualdehyde, using both alkali hydroxide and hydrogen chloride as condensing agents. In each case, a distinct condensation product was isolated. At present we are not in a position to offer an explanation of the apparent inactivity of *o*- and *p*-hydroxybenzaldehyde and deoxybenzoin in the presence of alkali hydroxide, but hope to deal with this point in a future communication.

#### EXPERIMENTAL.

##### *Attempted Condensation of Salicylaldehyde and Deoxybenzoin in the Presence of Alkali Hydroxide.*

1.2 Grams of salicylaldehyde and deoxybenzoin were dissolved in methyl alcohol, and to the mixture 3 grams of potassium hydroxide dissolved in 5 c.c. of water were added. The whole was then heated for two hours. A clear solution was obtained which, on the addition of water, gave a crystalline substance. This was collected, and the solution was acidified, but no solid substance separated.

*2:3-Diphenylbenzopyronium Chloride (I).*

A solution of 2 grams of deoxybenzoin and 1.2 grams of salicylaldehyde in methyl alcohol was saturated with dry hydrogen chloride. The colour of the solution changed from yellow to pink. It was kept overnight, but no precipitate separated. On the addition of very dilute hydrochloric acid, a dark red substance separated, which was dissolved in alcohol and reprecipitated by the addition of dilute hydrochloric acid, collected, washed with dilute hydrochloric acid, and kept in a vacuum over potassium hydroxide. On long keeping, it gradually became viscid. A portion of it, which was crystalline, was analysed:

0.1668 gave 0.4827  $\text{CO}_2$  and 0.0750  $\text{H}_2\text{O}$ .  $\text{C}=78.9$ ;  $\text{H}=5.0$ .

$\text{C}_{21}\text{H}_{15}\text{OCl}$  requires  $\text{C}=79.1$ ;  $\text{H}=4.7$  per cent.

The compound darkens at  $85^\circ$  and melts and decomposes at  $176^\circ$ .

*Attempted Condensation of p-Hydroxybenzaldehyde and Deoxybenzoin in the Presence of Alkali Hydroxide.*

A methyl-alcoholic solution of 1.2 grams of *p*-hydroxybenzaldehyde and 2 grams of deoxybenzoin was heated for about an hour with 3 grams of potassium hydroxide dissolved in 5 c.c. of water. A clear liquid was obtained, which was acidified as before, but nothing separated.

A condensation product was, however, obtained with hydrogen chloride as the condensing agent, but this compound could not be crystallised, and as it melted very indefinitely ( $170$ — $185^\circ$ ), it appeared to be a mixture which could not be easily separated.

 *$\alpha$ -p-Methoxybenzylidenedeoxybenzoin.*

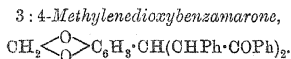
A current of dry hydrogen chloride was passed through a methyl-alcoholic solution of molecular quantities of anisaldehyde and deoxybenzoin for a few minutes. After allowing the solution to remain for two days, a crystalline substance separated, which was collected and recrystallised from alcohol. It separated in colourless needles melting at  $113^\circ$ . (Found:  $\text{C}=83.77$ ;  $\text{H}=5.8$ .  $\text{C}_{22}\text{H}_{18}\text{O}_2$  requires  $\text{C}=84.09$ ;  $\text{H}=5.70$  per cent.)

*p-Methoxy- $\alpha$ -chlorobenzyldeoxybenzoin.*

This was prepared by supersaturating a methyl-alcoholic solution of molecular quantities of anisaldehyde and deoxybenzoin with

dry hydrogen chloride. The substance began to separate at once from the solution, and was collected next day. It was recrystallised from acetic acid, when it separated in colourless needles melting and decomposing at  $152^{\circ}$  (Klages and Tetzner give  $144^{\circ}$ ). On testing the substance, it was found to contain chlorine. (Found: C=75.50; H=5.60.  $C_{22}H_{19}O_2Cl$  requires C=75.40; H=5.40 per cent.)

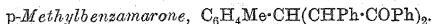
It may be noted here that 3:4-methylenedioxy- $\alpha$ -chlorobenzyldeoxybenzoin and *p*-methyl- $\alpha$ -chlorobenzyldeoxybenzoin were similarly obtained.



This was prepared by heating a methyl-alcoholic solution of 4 grams of deoxybenzoin and 1.5 grams of piperonal with 3 grams of potassium hydroxide dissolved in 5 c.c. of water. The substance which separated was collected, washed, and crystallised from acetic acid, when colourless needles melting at  $243-244^{\circ}$  were obtained:

0.1347 gave 0.4031  $CO_2$  and 0.0673  $H_2O$ . C=82.38; H=5.50.

$C_{30}H_{28}O_4$  requires C=82.40; H=5.30 per cent.



This was prepared by boiling a methyl-alcoholic solution of 1.2 grams of *p*-tolualdehyde and 4 grams of deoxybenzoin with 3 grams of potassium hydroxide in 5 c.c. of water. The substance crystallised from acetic acid in colourless needles melting at  $233-234^{\circ}$ :

0.1103 gave 0.3461  $CO_2$  and 0.0676  $H_2O$ . C=85.50; H=6.80.

$C_{30}H_{30}O_{2.2}H_2O$  requires C=85.80; H=6.30 per cent.

In conclusion, we beg to thank Principal F. W. Sudmersen for his keen interest in this work, and also the Chemical Society for a grant which has defrayed part of the expenditure.

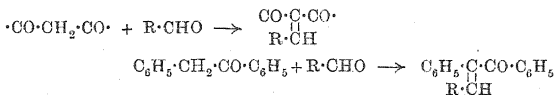
THE CHEMICAL LABORATORY,  
COTTON COLLEGE, GAUHATI  
ASSAM, INDIA.

[Received, January 13th, 1919.]

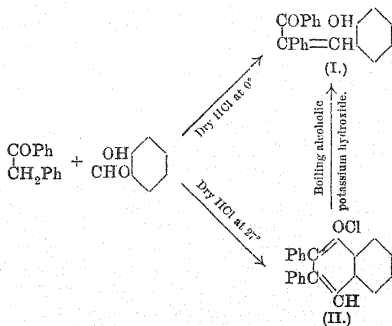
# LXV.—*Condensation of Deoxybenzoin with Aromatic Aldehydes.*

By BAWA KARTAR SINGH and JATINDRA KUMAR MAZUMDAR.

THIS work was undertaken with the object of extending the analogy which exists between deoxybenzoin and 1:3-diketones, inasmuch as both these substances may be condensed with aryl aldehydes by Knoevenagel's reaction. In the case of deoxybenzoin, it is the negative phenyl group that influences the reactivity of the hydrogen atoms of the methylene group, and thus acts similarly to one of the carbonyl groups in the 1:3-diketones:



With this object in view, several aryl aldehydes, namely, salicylaldehyde, *p*-hydroxybenzaldehyde, 2-naphthol-1-aldehyde, cinnamaldehyde, vanillin, *o*-aminobenzaldehyde, *p*-dimethylaminobenzaldehyde, piperonal, and *o*- and *p*-nitrobenzaldehyde\* were condensed with deoxybenzoin through the agency of hydrogen chloride, alcoholic potassium hydroxide, and diethylamine.



\* It was subsequently found that deoxybenzoin had already been condensed with piperonal, and *o*- and *p*-nitrobenzaldehyde by Stobbe and Wilson (*Annalen*, 1910, 374, 237); these compounds are therefore omitted from this paper.



In the course of this work, it has been observed that different results are obtained by condensing deoxybenzoin and salicylaldehyde with hydrogen chloride at  $0^{\circ}$  and at  $27^{\circ}$ . At  $0^{\circ}$ , salicylidenedeoxybenzoin (I) is obtained, whilst at  $27^{\circ}$  pyranol formation takes place, as previously observed by Decker and von Fellenberg (*Annalen*, 1909, **364**, 1). These authors isolated the product in the form of the ferrichloride, but we isolated the hydrochloride (II) direct.

#### EXPERIMENTAL.

##### *Salicylidenedeoxybenzoin (I).*

0.8 Gram of salicylaldehyde was mixed with an alcoholic solution of 1 gram of deoxybenzoin. The mixture was cooled in ice and saturated with dry hydrogen chloride, when the colour of the solution changed to dark brown. The mixture was kept for two to three days, when an amorphous, brown precipitate formed, which was collected and crystallised twice from dilute alcohol. The substance darkens at  $120^{\circ}$  and melts at  $160^{\circ}$ . It is soluble in alcohol or acetic acid, but insoluble in water:

0.1850 gave 0.5686  $\text{CO}_2$  and 0.1042  $\text{H}_2\text{O}$ .  $\text{C}=83.6$ ;  $\text{H}=6.0$ .

$\text{C}_{21}\text{H}_{16}\text{O}_2$  requires  $\text{C}=84.0$ ;  $\text{H}=5.40$  per cent.

0.2 Gram of the substance was boiled under reflux with 10 c.c. of 50 per cent. alcoholic potassium hydroxide for two hours. The substance dissolved with change of colour. On cooling and acidifying with dilute hydrochloric acid, the original substance was precipitated.

Condensation of salicylaldehyde with deoxybenzoin could not be effected through the agency of potassium hydroxide, although various methods were tried.

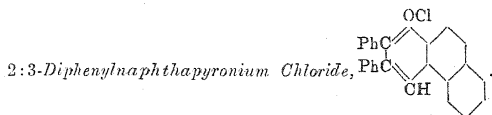
##### *2:3-Diphenylbenzopyryronium Chloride (II).*

1.5 Grams of salicylaldehyde were mixed with 2 grams of deoxybenzoin dissolved in a small quantity of methyl alcohol. Dry hydrogen chloride was then passed through the mixture for two hours at  $27^{\circ}$ ; a very bright deep red coloration was developed, and the solution acquired a syrupy consistency. On keeping for two days, red, needle-shaped crystals separated. They were collected and recrystallised from dilute acetic acid containing a little hydrochloric acid, when they formed red needles melting at  $100^{\circ}$ . The substance is soluble in alcohol or acetic acid, but insoluble in water:

0.1550 gave 0.4582  $\text{CO}_2$  and 0.0700  $\text{H}_2\text{O}$ .  $\text{C}=80.6$ ;  $\text{H}=5.0$ .

$\text{C}_{21}\text{H}_{15}\text{OCl}$  requires  $\text{C}=79.1$ ;  $\text{H}=4.7$  per cent.

0.5 Gram of the above pyranol compound was dissolved in alcohol and boiled under reflux with 20 c.c. of 10 per cent. alcoholic potassium hydroxide for three hours. The solution was then diluted with water and acidified with dilute acetic acid. The brown precipitate was collected, dissolved in alcohol, and again precipitated by water. It was identified as the compound (I), darkening at  $120^\circ$  and melting at  $160^\circ$ . (Found:  $\text{C}=83.5$ ;  $\text{H}=6.0$ .  $\text{C}_{21}\text{H}_{16}\text{O}_2$  requires  $\text{C}=84.0$ ;  $\text{H}=5.4$  per cent.)



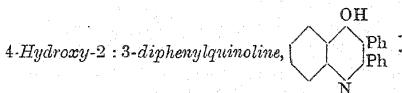
Two grams of deoxybenzoin and 1.6 grams of 2-naphthol-1-aldehyde were dissolved in methyl alcohol, and dry hydrogen chloride was passed into the solution for three hours at the ordinary temperature ( $25^\circ$ ). The solution gradually acquired a dark blue colour, and, after two to three days, dark blue needles separated. They were collected, washed with a little methyl alcohol, and recrystallised from dilute acetic acid, when they melted at  $148-150^\circ$ .

The compound is soluble in acetic acid, alcohol, or ether, but insoluble in water:

0.1255 gave 0.3738  $\text{CO}_2$  and 0.0566  $\text{H}_2\text{O}$ .  $\text{C}=81.16$ ;  $\text{H}=5.01$ .

$\text{C}_{25}\text{H}_{17}\text{OCl}$  requires  $\text{C}=81.41$ ;  $\text{H}=4.61$  per cent.

This substance decomposes gradually on keeping. It has been isolated in the form of the ferrichloride by Decker and von Fellenberg (*loc. cit.*).



Two grams of deoxybenzoin and 1.6 grams of anthranilic acid were mixed together, powdered, and heated in an oil-bath at  $130-150^\circ$  for three days. The product was then rendered alkaline with dilute sodium hydroxide solution and extracted with ether. The aqueous portion was acidified with dilute acetic acid and again extracted with ether. A solid gradually separated from

the aqueous solution. This was collected, washed, and crystallised from alcohol, when colourless, rectangular cubes melting at above  $300^{\circ}$  were obtained. The compound is insoluble in water, soluble in acetic acid or ether, and sparingly so in aqueous sodium hydroxide or alcohol:

0.1357 gave 5.8 c.c.  $N_2$  at  $32^{\circ}$  and 762 mm.  $N=4.8$ .

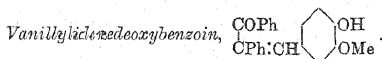
$C_{21}H_{15}ON$  requires  $N=4.53$  per cent.



*p*-Hydroxybenzaldehyde and deoxybenzoin in molecular proportion were dissolved in a small quantity of ethyl alcohol, and the solution was cooled in ice and saturated with dry hydrogen chloride, when a change of colour took place at once. On allowing the mixture to remain for two to three days, a precipitate gradually formed, which was collected and crystallised from dilute acetic acid, separating in red needles melting at  $155^{\circ}$ . The substance is soluble in alcohol or acetic acid, but insoluble in water. It does not contain chlorine:

0.1460 gave 0.4465  $\text{CO}_2$  and 0.0722  $\text{H}_2\text{O}$ .  $C=83.4$ ;  $H=5.5$ .

$C_{21}H_{16}O_2$  requires  $C=84.0$ ;  $H=5.4$  per cent.

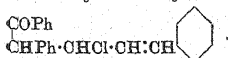


Vanillin and deoxybenzoin in molecular proportion were condensed as above, when an oil was obtained which solidified in three to four days. This separated from hot alcohol as an amorphous, reddish mass melting at  $146$ – $148^{\circ}$ . It is soluble in acetic acid, alcohol, or ether, but insoluble in water. It does not contain chlorine:

0.1274 gave 0.3755  $\text{CO}_2$  and 0.0596  $\text{H}_2\text{O}$ .  $C=80.4$ ;  $H=5.3$ .

$C_{22}H_{18}O_3$  requires  $C=80.0$ ;  $H=5.4$  per cent.

Cinnamylidenedeoxybenzoin hydrochloride,

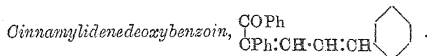


Deoxybenzoin and cinnamaldehyde in molecular proportion were condensed as above, and there was obtained a solid which separated from hot alcohol as an amorphous mass melting at  $100^{\circ}$ .

It is soluble in alcohol, acetic acid, or ether, but insoluble in water. The substance contains chlorine:

0.1238 gave 0.3609  $\text{CO}_2$  and 0.0657  $\text{H}_2\text{O}$ .  $\text{C}=79.5$ ;  $\text{H}=5.9$ .

$\text{C}_{23}\text{H}_{19}\text{OCl}$  requires  $\text{C}=79.7$ ;  $\text{H}=5.5$  per cent.

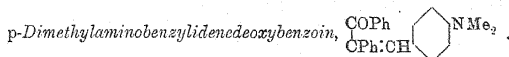


Deoxybenzoin and cinnamaldehyde in molecular proportion were dissolved in a little alcohol, and the mixture was cooled in ice, a few drops of diethylamine being added. A crystalline precipitate formed within an hour, which separated from hot glacial acetic acid in snow-white needles melting at  $145^\circ$ . The yield was almost theoretical.

It is insoluble in water and sparingly soluble in ethyl alcohol or acetic acid:

0.1095 gave 0.3558  $\text{CO}_2$  and 0.0601  $\text{H}_2\text{O}$ .  $\text{C}=88.6$ ;  $\text{H}=6.1$ .

$\text{C}_{23}\text{H}_{18}\text{O}$  requires  $\text{C}=89.0$ ;  $\text{H}=5.8$  per cent.



*p*-Dimethylaminobenzaldehyde and deoxybenzoin in molecular proportion were condensed in the usual manner, and a solid was obtained which crystallised from dilute acetic acid in colourless needles melting at  $98^\circ$ . It is very readily soluble in ethyl alcohol or acetic acid, but insoluble in water:

0.1159 gave 4.6 c.c.  $\text{N}_2$  at  $28^\circ$  and 761 mm.  $\text{N}=4.6$ .

$\text{C}_{23}\text{H}_{21}\text{ON}$  requires  $\text{N}=4.3$  per cent.

This work was carried out at Dacca College in 1917.

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[Received, February 6th, 1919.]

# LXVI.—*Trustworthiness of the Balance over Long Periods of Time.*

By GEORGE DEAN.

DURING the prosecution of a series of atomic-weight determinations by the author, a paper was published on "The limitations of the balance" (Blount, T., 1917, 111, 1035). The author there draws the conclusion, based on experiments with several balances, that although weighings of a given object made within a few hours—or even days—of each other may be concordant, this is not the case if they are extended over several months. A variation as high as 1.6 milligrams was detected, and attributed to the gradual shifting of the central knife edge.

If this conclusion is established, the accuracy of many atomic-weight determinations will be seriously impaired. The work referred to above is especially liable to this error, as a period of three to fifteen months intervened between the initial and final weighings. Fortunately, it was possible to test the magnitude of the error in this case. The experiments were carried out in weighed silica flasks, each provided with a similar silica flask as counterpoise. These were used in successive experiments, and, being appreciably affected by the chemical action, their weights, recorded during several years, were useless for the present purpose. One flask, however, being of inconvenient shape, had been used, re-weighed, and rejected. It was weighed after long intervals. The details of the weighings are as follows, the numbers representing the weights added to the counterpoise to make it balance the flask.

May 17th, 1917. Flask treated with boiling nitric acid, washed with distilled water, dried, wiped, ignited, cooled in desiccator with counter, and both left on pans of balance before weighing	+0.001300 gram	} 0.001312 gram.
May 18th, 1917. Merely replaced in balance and left all night before weighing	+0.001325 ,,	

The two were now left over calcium chloride under a bell glass for ten months.

Mar. 7th, 1918. Replaced in balance, left all night and re-weighed	+0.001360 gram	} 0.001374 gram.
Mar. 8th, 1918. Flask and counter, both carefully wiped and replaced, left all night on pans before weighing	+0.001379 ,,	
Mar. 9th, 1918. Merely replaced and left all night	+0.001382 ,,	

After a further interval of two months, a single weighing was taken:

July 23rd, 1918. Flask, etc., replaced in balance and left all night . . . . . 0.001415 gram.

The flasks were now left in the desiccator for ten months, the balance remaining practically unused:

May 20th, 1919.	Replaced in balance and left all night . . . . .	+ 0.001422 gram	
„ 23rd „	Flask wiped and heated (but not counter), cooled in desiccator, in balance all night . . . . .	+ 0.001419 „	
„ 26th „	Both replaced in balance and left for week-end . . . . .	+ 0.001406 „	
„ 27th „	Counterpoise, wiped, ignited, cooled in desiccator, both left in balance all night . . . . .	+ 0.001474 „	0.001435 gram.
„ 28th „	Both replaced in balance and left all night . . . . .	+ 0.001480 „	
„ 31st „	Both in desiccator 2 days, in balance 1 night . . . . .	+ 0.001421 „	
June 3rd „	Both in desiccator 2 days, in balance 1 night . . . . .	+ 0.001425 „	

The total variation in weight of a flask weighing 40.65 grams, in two years, is thus + 0.000123 gram, made up of + 0.000062 gram in the first ten months, + 0.000041 gram in the succeeding four months, and 0.000020 gram in the final ten months.

After carrying out determinations extending over several years, and depending on some thousands of elaborate weighings, it was satisfactory to find the error introduced by the duration of an experiment was so small as to be practically negligible. The fact that the variation was a steady increase rather favours the view that it is due to a displacement of the knife edge.

The test was more searching than if twin metal weights had been used; the flasks were more bulky; they were polished occasionally by breathing upon them and rubbing with a cloth, this being necessary in the atomic-weight experiments to remove a slight film deposited on the flask from the oven in which it was heated. As each flask had an external surface of about 250 sq. cm., there is a possibility of changes in weight from this treatment, as also from air condensation after heating.

The weighings were not made under ideal conditions. The room is small and has a low ceiling, with two doors and windows, is heated by a steam radiator, and subject to vibration from a ventilating fan. To minimise these drawbacks, the flasks were placed on the balance the night before the weighing, the windows

heavily curtained, and fan and radiator turned off. In this way, trustworthy readings were secured.

The method of swings was used, ten swings of the pointer to the left and nine to the right being recorded, and the point of equilibrium on the scale calculated. The rider was next shifted along the beam to increase the weight by 1 milligram, and the observations were repeated. Finally, the flasks and rider were removed from the balance, which was then left for at least an hour. It was then set swinging, and the true "zero" of the empty balance worked out. From the three equilibrium positions, the weight of the flask is easily calculated. It was necessary to adopt this tedious method, as the "zero" of the balance is rarely constant for more than a few hours at a time.

The balance was an ordinary short-beam instrument of (unknown) German make. It was in constant use except during the final ten months, when no weighings were made on it except those recorded above.

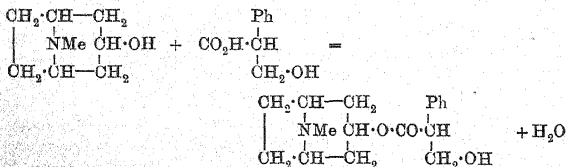
CHEMICAL DEPARTMENT,  
WEST HAM MUNICIPAL  
TECHNICAL INSTITUTE.

[Received, June 10th, 1919.]

## LXVII.—*The Isomeric Tropic Acids.*

By ALEX. MCKENZIE and JOHN KERFOOT WOOD.

ALTHOUGH nearly forty years have elapsed since Ladenburg carried out his fundamental researches on the constitution of atropine, this alkaloid is still obtained exclusively from natural sources. This is undoubtedly due to the difficulties involved in the preparation in quantity of the two constituents of the atropine molecule, namely, tropine and *r*-tropic acid. The yield of atropine obtained by Ladenburg by the combination of the two constituents according to the equation

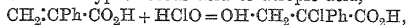


was apparently very small. Wolfenstein and Mamlock (*Ber.*, 1908, 41, 723) have, however, shown that by acetylating tropic

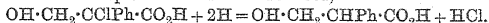
acid, then converting into the acid chloride, and combining this with tropine, a good yield of acetyl tropine hydrochloride can be obtained, and from the latter compound the acetyl group can be eliminated with the formation of atropine in a satisfactory yield. In the light of the experience of these authors, there should be no difficulty in effecting the synthesis of atropine in fair quantity provided that methods are available for the production of the requisite tropine and tropic acid.

The recent synthesis of tropinone by Robinson (T., 1917, 111, 762) suggests the possibility of the production of synthetic tropine. Meanwhile, the present authors had been engaged in the examination of various methods for the preparation of tropic acid other than that from atropine itself, and the results are described in the present communication.

Ladenburg and Rügheimer (*Ber.*, 1880, 13, 373; *Annalen*, 1883, 217, 74) claim to have converted atropic acid into tropic acid in the following manner. Chlorotropic acid was first obtained by the direct addition of hypochlorous acid to atropic acid,



and the chlorotropic acid was then reduced,



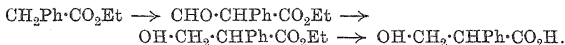
It is apparent from Ladenburg's description that some difficulty was experienced by him in the reduction of the chlorotropic acid, although it is stated that the action proceeded smoothly when a mixture of zinc dust and iron filings was added to a solution of the acid in concentrated potassium hydroxide. It may be stated at once that our experience with this method was most disappointing. There was no difficulty in preparing the chloro-acid, but all our attempts to reduce it to tropic acid, whether by Ladenburg's method or in other ways, ended in failure. In many of these experiments the chloro-acid was partly recovered, whilst in one or two cases the product was free from halogen and possessed the melting point of atroglyceric acid. In view of the difficulties encountered, we drew the conclusion that this method is not a practical one for the preparation of appreciable quantities of tropic acid.

Spiegel (*Ber.*, 1881, 14, 235) obtained tropic acid by heating acetophenonecyanohydrin with hydrochloric acid at 130°, and then acting on the resulting  $\beta$ -chlorohydratropic acid with a solution of sodium carbonate at 120°. There are no details quoted in the paper regarding the yield of tropic acid.

A method which we employed was the reduction of the formylphenylacetic ester, prepared by Wislicenus's method, from ethyl formate and ethyl phenylacetate. This ester was reduced in

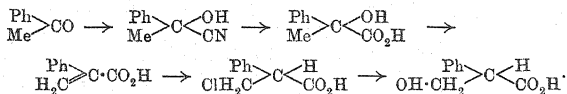


etheral solution by means of aluminium amalgam, and the resulting tropic ester was hydrolysed:



After these experiments were completed by us, the method was described by Müller (*Ber.*, 1918, **51**, 252; D.R.-P. 302737), and also by Wislicenus and Billhuber (*Ber.*, 1918, **51**, 1237), the latter chemists having used methyl formylphenylacetate. Müller states that the aluminium residue retains almost half of the formyl ester, which is therefore not reduced, and, according to him, cannot be removed from the residue by means of ether. Wislicenus and Billhuber also noticed that a portion of the formyl ester was retained by the aluminium. We also obtained a small yield of tropic acid by this process.

Of the methods we have studied for the preparation of tropic acid, the following gave by far the best result. Acetophenone was converted into atrolactic acid, which, on being heated under diminished pressure, gave atropic acid; this in turn was converted into  $\beta$ -chlorohydratropic acid by the action of hydrogen chloride on its ethereal solution, and the halogen was then displaced by boiling the acid with an aqueous solution of sodium carbonate:



The resolution of *r*-tropic acid into its optically active components is described by Ladenburg and Hundt (*Ber.*, 1889, **22**, 2591). The acid was dissolved in dilute aqueous alcohol and neutralised by quinine. The resulting salt was crystallised until the melting point was constant, the value 186—187° being given. The tropic acid obtained from this salt melted at 127—128°, and gave  $[\alpha]_D +71.4^\circ$  "als Mittel aus Versuchen in verschieden concentrirten Lösungen." This value for the specific rotatory power of the *d*-acid has no significance, since the solvent employed is not quoted.

Amenomiya (*Arch. Pharm.*, 1902, **240**, 498) acted on a mixture of 10 grams of atropine and *l*-hyoscyamine with water, and obtained a mixture of *r*-tropic acid and a small quantity of the *l*-isomeride. This was neutralised with quinine, and the resolution conducted according to Ladenburg and Hundt. The quinine *d*-salt melted at 189—190°. The resulting acid was washed with benzene to free it from atropic acid; it then melted at 126—127°, whilst the value

$[\alpha]_D^{20} + 71.3^\circ$  for  $c=2.384$  in ethyl-alcoholic solution is quoted. From the mother liquors of the quinine salt, a levorotatory tropic acid melting at  $126^\circ$  and giving  $[\alpha]_D^{20} - 72.75^\circ$  in aqueous solution was prepared. No analyses of the optically active acids are quoted either by Ladenburg and Hundt or by Amenomiya. Moreover, the quantity of inactive acid at the disposal of those investigators would seem to have been rather inadequate for the purpose they had in view.

Atropine is the *dl*-tropyl ester of tropine, whilst *l*-hyoscyamine is the *l*-tropyl ester of tropine. Hyoscyamine has the grouping  $\cdot\text{CO}\cdot\text{CH}\cdot$ ; and, in accordance with the work carried out by one of us and his co-workers on racemisation with alcoholic alkali, it might be expected that this alkaloid would undergo racemisation with alcoholic alkali. Data in the literature show that this is the case, but the point is perhaps worthy of further investigation. Pure atropine is optically inactive, but the atropine of commerce is often slightly levorotatory, owing to its containing some hyoscyamine. In all probability, the plant builds up the pure *l*-hyoscyamine, and this is racemised either in the plant itself or during the commercial preparation of atropine. The question (which probably has received attention from the manufacturers of atropine) suggests itself: Would it be possible to isolate pure hyoscyamine from the plant, or would this compound racemise so readily that its isolation on the large scale would be impossible? One of the sources of atropine is *Hyoscyamus muticus*—which is said to contain hyoscyamine only. Now it is significant that alkali always appears to be used in the extraction of atropine from plants. It might be possible technically to avoid the use of alkali in the extraction, and thus obtain a salt of pure hyoscyamine. If this were practical, the advantage would be very great, since *l*-hyoscyamine in its mydriatic power is reported as being one hundred times as active as its *d*-isomeride. It would therefore be a much better mydriatic than atropine. Similar considerations apply to pilocarpine. It has, however, to be recognised that it is doubtful if the naturally occurring *l*-hyoscyamine or its *d*-isomeride has ever been prepared in a state of purity, and it seems very probable that Barrowcliff and Tutin (T., 1909, 95, 1966) are correct when they suggest that the interesting physiological results of Cushny on the comparison of the *d*- and *l*-hyoscyamines were obtained with alkaloids which were not optically pure.

By the hydrolysis of *l*-hyoscyamine, Gadamer (*Arch. Pharm.*, 1901, 239, 294) obtained a levorotatory tropic acid melting at  $123$ – $124^\circ$  and having  $[\alpha]_D^{20} - 69.49^\circ$  in aqueous solution. A purer specimen was obtained by heating an aqueous solution of *l*-hyoscine;

the resulting acid was washed with benzene to free it from the small amount of atropic acid present, and the residue then crystallised from water. The resulting tropic acid melted at 125—126° and gave  $[\alpha]_D -71.81^\circ$  in aqueous solution.

As it appeared to the present authors to be of some importance to establish the purity of the *d*- and *l*-tropic acids, the resolution of the *r*-acid was carried out as described in the experimental portion of this paper. The *d*-acid was obtained by means of quinine, the solvent used being ethyl alcohol. It melted at 128—129° and had  $[\alpha]_D^{15} +72.2^\circ$  for  $c=2.695$  in ethyl-alcoholic solution, a result which is nearly identical with that of Amenomiya, who found  $[\alpha]_D +71.3^\circ$ . We obtained the *l*-acid by means of morphine, the solvent being ethyl alcohol. This acid melted at 128—129°, and had  $[\alpha]_D^{15} -72.5^\circ$  for  $c=2.578$  in ethyl-alcoholic solution and  $[\alpha]_D^{15} -79.0^\circ$  for  $c=1.538$  in aqueous solution. The laevorotatory acid of Amenomiya, which gave  $[\alpha]_D -72.75^\circ$  in aqueous solution, and Gadamer's acid, with  $[\alpha]_D -69.49^\circ$  in aqueous solution, were therefore not optically pure.

The results described in the present paper were practically completed towards the end of 1917, but publication has been delayed owing to the pressure of other work. Since the present paper was written, King (this vol., p. 476) has described the resolution of tropic acid, and our values for the specific rotatory powers of the optically active acids are in close agreement with those given by him. It is therefore satisfactory that the constants for these important acids have at last been definitely settled.

## EXPERIMENTAL.

### *Reduction of Ethyl Formylphenylacetate.*

As the reduction of this ester has already been described in the literature, it is unnecessary to describe our experience of the method. The ester used was the liquid modification, which was prepared by the action of sodium on a mixture of ethyl phenylacetate and ethyl formate, and purified through the copper derivative, as described by Wislicenus. In the bulk of the experiments, the reducing agent employed was aluminium amalgam. The ester was also reduced by the action of sodium on a solution of the ester in glacial acetic acid. The yields of the pure recrystallised tropic acid varied from 16 to 30 per cent. of the theoretical, calculating from the phenylformylacetic ester used.

*Preparation of Atrolactic Acid.*

This acid was prepared as described by McKenzie and Clough (T., 1912, 101, 393). The following details of a typical preparation may be given.

To a mixture of 80 grams of potassium cyanide (98 per cent.), 100 grams of acetophenone, and 5 c.c. of water, fuming hydrochloric acid (D 1.2) was added from a dropping funnel at the rate of twelve to fifteen drops at a time, the mixture being shaken vigorously after each addition. This operation lasted for five hours, 15 c.c. of acid being added in each of the first two hours and 20 c.c. in each of the subsequent hours. During the first three hours, the mixture was maintained at the ordinary temperature, so that the acetophenone did not solidify, but towards the close it was cooled in ice-cold water. When the addition of the acid was complete, the mixture was allowed to remain for half an hour, and the oil then poured off and washed with water. A further small quantity of oil was obtained by adding water to the sludge left in the reaction flask. The oil was then poured into 200 c.c. of hydrochloric acid (D 1.2) and left overnight. Sodium hydroxide solution was added until the solution was neutral, and then three times the theoretical amount of the same alkali (calculated on the acetophenone used) was added, and the mixture distilled in a current of steam until the evolution of ammonia ceased. About 65 grams of acetophenone were recovered. The contents of the distillation flask were evaporated until the separation of solid started. On cooling, the crystals were separated and acidified with hydrochloric acid, using Congo-red as indicator. The atrolactic acid was filtered off, the filtrate evaporated further, and cooled; the resulting crystals contained some sodium chloride, from which the acid was separated by means of ether. Some additional acid was obtained from the filtrates. The ethereal solution of the acid was dried with anhydrous magnesium sulphate, the ether expelled, and the atrolactic acid crystallised from water. The yield was 35 grams of crystallised acid, and this corresponds with a yield of 73 per cent. on the acetophenone converted.

Professor Kipping kindly suggested to us a modification of this method which gives good results. After the cyanohydrin was hydrolysed, water was added, and the acetophenone removed by distillation in steam. The hot acid solution was then filtered and cooled, when atrolactic acid separated. A further quantity can be obtained by extracting the filtrate with ether. In employing this method, it should, however, be borne in mind that sufficient water must be added after the hydrolysis of the cyanohydrin, and

that the subsequent heating in the presence of hydrochloric acid should not be unduly prolonged, otherwise the atrolactic acid may be partly converted into atropic acid. Ladenburg and Rügheimer (*loc. cit.*) have pointed out that when atrolactic acid is boiled under a reflux condenser with moderately dilute hydrochloric acid for some time, then diluted with water, and distilled, small quantities of atropic acid pass over with the steam. With more concentrated hydrochloric acid, appreciable quantities of *isoatropic* acid are formed.

#### *Preparation of Atropic Acid.*

The process of Ladenburg and Rügheimer, to which reference has just been made, is not a convenient one for the preparation of atropic acid in quantity. Moreover, the method described by Kraut (*Annalen*, 1863, **128**, 282; compare also Fittig and Wurster, *Annalen*, 1879, **195**, 147), whereby atropine is boiled with barium hydroxide, is not very practical when the expense of atropine is considered, and the same criticism may be passed on Lossen's method of heating atropine with fuming hydrochloric acid at 120—130° (*Annalen*, 1866, **138**, 132).

We found that atrolactic acid can be converted into atropic acid by distillation under diminished pressure. Atrolactic acid contains water of crystallisation, but it is not necessary to dehydrate the acid before submitting it to distillation. The method is a convenient one, but certain precautions require to be taken in order to secure a good yield. The chief difficulty arose from the ease with which atropic acid is transformed under the agency of heat into  $\alpha$ - and  $\beta$ -*isoatropic* acids (Fittig and Wurster, *loc. cit.*). We carried out the distillation in a silica flask with a capacity of 110 c.c. and provided with a side-tube of 12 mm. internal diameter and 28 cm. in length. The side-tube acts as a suitable condenser, and there is no danger of it becoming choked owing to the solidification of the condensed atropic acid, as is the case when an ordinary distilling flask is used. Experience showed that it is very advisable to heat the atrolactic acid with a free flame rather than to use an oil-bath. If the distillation is carried out too slowly, a viscous residue of the *isoatropic* acids is left in the distilling flask, and the yield of atropic acid is poor. On the other hand, if the operation is conducted too rapidly, some atrolactic acid passes over along with the atropic acid; the two acids are, however, easily separated by taking advantage of their very different solubilities in water, atropic acid dissolving, according to Kraut, in 692.5 parts of water at 19.1°, whilst the solubility of

atrolactic acid was found by Lennart Smith (*J. pr. Chem.*, 1911, [ii], **84**, 737) to be 17.04 parts per litre of water at 18°. Under a pressure of 10—15 mm., an oil distils at 177—179° and solidifies quickly. The distillate is dissolved in a warm mixture of ethyl alcohol and water, and hot water is then added until the liquid becomes cloudy. The atropic acid separates on cooling in the form of iridescent leaflets. Should the melting point of the dried crystals indicate that the atropic acid is not quite pure, the crystals are left for some time in contact with water in order to remove atrolactic acid.

The results of three experiments may be given:

- (1) Nineteen grams of dehydrated atrolactic acid gave 12 grams of atropic acid.
- (2) Twenty grams of dehydrated atrolactic acid gave 13 grams of atropic acid.
- (3) Twenty-one grams of dehydrated atrolactic acid gave 13.5 grams of atropic acid.

The time of distillation was fifteen minutes. The mean yield from the above figures is 72 per cent. of the theoretical; a further small quantity of atropic acid may be obtained from the mother liquors.

The acid melts at 106—107°. It gave  $C=73.0$ ;  $H=5.5$ . (Calc.:  $C=73.0$ ;  $H=5.4$  per cent.)

This is a much more practical method for preparing atropic acid than that described by Ladenburg and Rügheimer (*Ber.*, 1880, **13**, 2041), who also used acetophenone as the starting point. They formed acetophenone dichloride,  $CMePhCl_2$ , which, by means of potassium cyanide and ethyl alcohol, was converted into the nitrile,  $CMePh(CN) \cdot OEt$ , and this, on hydrolysis by baryta, gave the barium salt of ethyl atrolactic acid,  $CMePh(CO_2H) \cdot OEt$ . Atropic acid was obtained from the latter acid by treatment with concentrated hydrochloric acid. The method now described is also more practical than Spiegel's method, whereby atropic acid is produced by boiling  $\beta$ -chlorohydratropic acid with aqueous sodium hydroxide.

#### *Preparation of $\beta$ -Chlorohydratropic Acid.*

An interesting study of the additive compounds of atropic acid and the halogen acids is described by Merling, who obtained  $\beta$ -chlorohydratropic acid by heating atropic acid with fuming hydrochloric acid in a sealed tube at 100° for five hours (*Annalen*, 1881, **209**, 1). The yield of the chloro-acid is not stated, but it is certain that the method is not a practical one, as atropic acid

would, under the experimental conditions, undergo considerable transformation into the *isoatropic* acids, and the formation of these acids is indicated in Merling's description.

The following is a convenient method for preparing  $\beta$ -chlorohydratropic acid. Ten grams of atropic acid were dissolved in 200 c.c. of dry ether free from alcohol, and a current of dry hydrogen chloride was passed in slowly for about two hours. The solution was kept warm during this period, the flask containing it having been attached to a reflux condenser provided with a calcium chloride drying tube. The solution was then kept overnight, and the hydrogen chloride again passed through the warm solution next day for four to five hours. After the bulk of the ether was removed by distillation, the residual liquid was allowed to evaporate spontaneously. An almost completely solid residue was obtained which, after two crystallisations from carbon disulphide, was sufficiently pure for analysis. Only one crystallisation is necessary when the chloro-acid is to be used for conversion into tropic acid. The acid melted at 88–89°, whereas Merling gives 87–88°. (Found: Cl=19.3. Calc.: Cl=19.2 per cent.)

Ten grams of atropic acid gave 10 grams of the chloro-acid, a yield of 80 per cent. of the theoretical.

#### *Conversion of $\beta$ -Chlorohydratropic Acid into Tropic Acid.*

Merling (*loc. cit.*) found that the chloro-acid could be hydrolysed by heating with a solution of potassium carbonate. The present authors have examined the hydrolysis under various conditions with the object of securing as good a yield of tropic acid as possible, since certain secondary reactions are liable to occur. Those reactions are (a) the tendency for the formation of styrene through the elimination of hydrogen chloride and carbon dioxide, as observed by Merling, and (b) the readiness with which tropic acid in the presence of alkalis loses water and passes into atropic acid (Hesse, *J. pr. Chem.*, 1901, [ii], 64, 286). The action of water alone was found to be unsatisfactory, but better results were obtained with aqueous sodium carbonate. The amount of sodium carbonate used was rather less than would be required to neutralise the original acid and the hydrochloric acid formed during the hydrolysis; there was practically no difference in the yield whether all the sodium carbonate was added at the beginning or gradually during the time of boiling. As an example, the following experiment may be quoted.

Four grams of the chloro-acid were mixed with 80 c.c. of water, and the mixture was boiled under a reflux condenser. A solution

of sodium carbonate (1.73*N*) was run in slowly, the boiling being maintained; 24.1 c.c. were added in the course of fifteen minutes, the boiling being then continued for a further three and a-half hours without the addition of any further quantity of alkali. On cooling, the solution was faintly alkaline; it was extracted with ether to remove styrene, acidified with dilute sulphuric acid, and extracted five times with ether. The ethereal solution was dried with sodium sulphate, and to the oily residue which remained after the removal of the ether, benzene was added. The resulting crystals were separated, washed with benzene, and dried. The yield was 2.32 grams and the melting point 116—117°. The aqueous solution which had been extracted with ether gave an additional 0.2 gram of tropic acid when extracted for five hours in a continuous extractor. Yield=70 per cent. Equivalent: Found: 166.6. Calc.: 166.1.

The residue obtained by the evaporation of the benzene filtrates reduced alkaline permanganate strongly, and doubtless consisted of a mixture of atropic and tropic acids.

In a similar experiment, using 10 grams of the chloro-acid, the yield of tropic acid amounted to 61 per cent. of the theoretical.

The tropic acid obtained in this manner was free from atropic acid.

The yield was smaller when sodium hydroxide was used in place of sodium carbonate. Solutions of sodium acetate and silver nitrate were also employed as hydrolysing agents, but in neither case was the yield of tropic acid so good as when sodium carbonate was used.

Attempts were made to study the hydrolysis from the kinetic point of view, but for various reasons these proved unsuccessful. At the boiling point, the reaction takes place too rapidly to permit of accurate determinations of the velocity of reaction, whilst at lower temperatures the solubility of the acid in water is too small. An attempt was made to overcome the latter difficulty by using a mixture of alcohol and water as the solvent, but under these conditions the velocity of reaction was reduced to such small dimensions as to be impossible of accurate determination.

#### *Attempts to Reduce Chlorotropic Acid.*

The method described by Ladenburg and Rügheimer for the preparation of chlorotropic acid was followed. The chlorotropic acid obtained melted at 129—130°, in agreement with the value given by Ladenburg, namely, 128—130°.

Reference has already been made in the theoretical portion of



the paper to the failure which attended our numerous efforts to reduce chlorotropic acid to tropic acid. Ladenburg describes the action as taking place when zinc dust and iron filings are added to a solution of the acid in a concentrated aqueous solution of potassium hydroxide, but no information is given regarding the actual concentration of the alkali he used. We made numerous experiments, using alkaline solutions of different concentrations. When the chlorotropic acid was dissolved in a solution of sodium or potassium hydroxide containing 20 grams of alkali in 100 c.c. of water and left for several days in contact with zinc dust and iron filings, the product which was obtained after the removal of the dissolved zinc and the extraction of the acidified portion by means of ether was a substance of indefinite melting point, and still contained chlorine. With a more concentrated solution of alkali (10 grams of potassium hydroxide in 10 grams of water), the product was free from chlorine. It appeared to be a mixture, as it had a strong reducing action on alkaline permanganate, but on treatment with benzene, part of it was sparingly soluble, and this, after washing with benzene, was practically devoid of reducing action. It was soluble in water, melted at  $144-146^{\circ}$ , and was probably atroglyceric acid, which melts, according to Fittig and Kast (*Annalen*, 1881, 206, 32), at  $146^{\circ}$ .

Other reducing agents which were tried were sodium amalgam, zinc and hydrochloric acid, sodium hydroxide and aluminium powder, and aluminium amalgam. In each case, chlorotropic acid was recovered.

#### *Preparation of the Optically Active Tropic Acids.*

85.4 Grams of hydrated quinine (1 mol.) were dissolved in 850 c.c. of absolute ethyl alcohol at  $17^{\circ}$ , and 37.5 grams of *r*-tropic acid (1 mol.) were added with stirring until the solution was homogeneous. Crystallisation began after five minutes, and proceeded rapidly. After nineteen hours at the ordinary temperature, the crystals were separated; after remaining on a porous plate for three days, they amounted to 71 grams. Crystallisation was carried out another eight times from ethyl alcohol. The alcohol was distilled off from the filtrate from each successive crystallisation, the residue decomposed by dilute sulphuric acid, and the tropic acid extracted with ether and dried with sodium sulphate. The progress of the resolution was indicated by determining the specific rotatory power of the successive acids in ethyl-alcoholic solution, the following values for  $[\alpha]_D$  being obtained:  $-54.2^{\circ}$ ,  $-36.7^{\circ}$ ,  $-6.1^{\circ}$ ,  $+23.1^{\circ}$ ,  $+41.2^{\circ}$ ,  $+60.8^{\circ}$ ,  $+67.1^{\circ}$ ,  $+69.4^{\circ}$ ,

+69.6°. The quinine *d*-salt amounted to 25.5 grams; it separated from ethyl alcohol in felted leaflets grouped in rosettes melting at 190—191°; 100 c.c. of its ethyl-alcoholic solution contain about 0.55 gram of the salt at 13°. The salt was decomposed by dilute sulphuric acid, and the tropic acid repeatedly extracted with ether, 7.2 grams of pure *d*-acid being obtained.

*d*-Tropic acid is sparingly soluble in benzene, from which it separates in lustrous needles melting at 128—129°. It crystallises from water in glassy needles and plates grouped in rosettes:

0.1858 gave 0.4421 CO<sub>2</sub> and 0.1043 H<sub>2</sub>O. C=64.9; H=6.3.

C<sub>9</sub>H<sub>10</sub>O<sub>3</sub> requires C=65.0; H=6.1 per cent.

Its specific rotation was determined in the following solvents:

(a) Ethyl alcohol:

$$c = 2.695, l = 2; \alpha_D^{16} + 3.89^\circ; [\alpha]_D^{16} + 72.2^\circ.$$

(b) Water:

$$c = 1.515, l = 2; \alpha_D^{16} + 2.43^\circ; [\alpha]_D^{16} + 80.2^\circ.$$

(c) Acetone:

$$c = 2.19, l = 2; \alpha_D^{13} + 3.67^\circ; [\alpha]_D^{13} + 83.8^\circ.$$

For the preparation of the *l*-isomeride, 9 grams of acid with  $[\alpha]_D - 54.2^\circ$  for  $c = 2.65$  in ethyl-alcoholic solution, and 4 grams of acid with  $[\alpha]_D - 36.7^\circ$  for  $c = 2.574$  in ethyl-alcoholic solution (obtained from the first two filtrates in the resolution just described), were united and added to a warm solution of 23.8 grams of morphine in 350 c.c. of ethyl alcohol. On cooling, glassy crystals began to separate, and these were collected on the following day. The product, dried in air at the ordinary temperature, amounted to 32.5 grams. It was crystallised from ethyl alcohol six times. The tropic acid recovered from the mother liquors from these crystallisations gave the following values for  $[\alpha]_D$  in ethyl-alcoholic solution:  $-13.5^\circ$ ,  $-28^\circ$ ,  $-56^\circ$ ,  $-59.4^\circ$ ,  $-60.7^\circ$ ,  $-63^\circ$ . Although the morphine salt (14 grams) was not yet quite pure, it was deemed advisable at this stage to decompose it with dilute sulphuric acid. The resulting acid (4 grams) was nearly pure, giving the value  $[\alpha]_D - 71.3^\circ$  in ethyl-alcoholic solution. The pure acid was obtained after one crystallisation from water.

*l*-Tropic acid melts at 128—129°. Equivalent: Found: 166.5. Calc.: 166.1. The values for its rotatory power were determined in the following solvents, and are in agreement with the corresponding values for its *d*-isomeride:

(a) Ethyl alcohol:

$$c = 2.578, l = 2; \alpha_D^{13} - 3.74^\circ; [\alpha]_D^{13} - 72.5^\circ.$$

(b) Water:

$$c = 1.538, l = 2; \alpha_D^{15} - 2.43^\circ; [\alpha]_D^{15} - 79.0^\circ.$$

(c) Acetone:

$$c = 1.806, l = 2; \alpha_D^{15} - 3.01^\circ; [\alpha]_D^{15} - 83.3^\circ.$$

The authors desire to acknowledge the able assistance rendered by the late Mr. Harold Halcro Johnston, B.Sc., in the earlier stages of this research. They are also indebted to Professors G. G. Henderson and F. S. Kipping for a supply of atrolactic acid.

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## LXVIII.—*The Absorption Spectra of the Nitric Esters of Glycerol.*

By HARRY HEPWORTH.

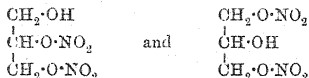
IN 1906, Kast (*Zeitsch. ges. Schiess- u. Sprengstoffw.*, 1906, 1, 225) discovered that nitroglycerin or glyceryl trinitrate is capable of existing in two isomeric forms in the solid state, a labile isomeride melting at  $2.8^\circ$  and a stable form melting at  $13.5^\circ$ . In a later paper on this subject by Nauckhoff (*ibid.*, 1911, 6, 124), in which a description of the crystalline structure of the isomeride of higher melting point is given, the author differs from Kast in being unable to isolate the isomeride of lower melting point. The question of the existence of a second solid form of nitroglycerin has been carefully investigated by Hibbert ("Eighth International Congress of Applied Chemistry," 1912, 4, 37), who has not only confirmed the existence of two solid isomerides, but has also investigated the various conditions under which each may be obtained.

Hibbert has compared these two solid isomerides with the two isomeric forms of benzophenone, and although he justly points out that structural isomerism is theoretically possible, yet on the whole the evidence points to the two forms of nitroglycerin being physical isomerides one of the other. This conclusion is largely based on the views of Schaum (*Annalen*, 1898, 300, 209), according to whom the criterion between chemical and physical isomerism is to be found in the fact that with purely physical isomerides, inoculation of the solid labile with the solid stable form brings about the complete conversion of the former in the absence of any solvent.

Now it is evident that if the two solid forms of nitroglycerin are to be represented by two different structural formulæ, then the labile and stable forms should give rise to two different chemical compounds, either in the liquid state or in solution, and it is reasonable to suppose that these solutions will exhibit different absorption spectra. Aqueous solutions of nitroglycerin derived from the two forms have been examined spectrographically, and found to give identical spectra (Fig. 1), from which it is clear that there is no evidence of chemical isomerism in solution, and that the labile and solid forms of nitroglycerin are to be regarded as physical isomerides. Since the nitroglycerins examined showed general absorption only, it is improbable that an equilibrium mixture of dynamic isomerides is obtained when either form is dissolved in water.

The absorption spectrum of a sample of commercial nitroglycerin has also been determined as a matter of interest. It will be observed (Fig. 1) that the latter is much more absorptive than pure nitroglycerin. This cannot be due to the presence of lower nitrates, as the latter are soluble in water.

The lower nitrates of glycerol have been investigated by Will (*Ber.*, 1908, 41, 1107), and the glyceryl  $\alpha\beta$ - and  $\alpha\gamma$ -dinitrates were prepared and separated as described by him. It is evident that in the case of the dinitrates, the two isomerides may have the structural formulæ



and should therefore give rise to two different absorption spectra. The absorption in aqueous solution was investigated, with the results shown in Fig. 2. It will be observed that the  $\alpha\beta$ -ester shows the stronger absorption, and this would be expected from the fact that this ester is more unsymmetrical than the  $\alpha\gamma$ -dinitrate. Both isomerides show less absorption than nitroglycerin.

A sample of  $\alpha$ -methylin dinitrate was kindly provided by Mr. D. T. Jones, and had been prepared by the nitration of glyceryl  $\alpha$ -monomethyl ether (Jones, T., 1919, 115, 76). This sample had a faint yellow colour, and was fractionally crystallised before use. The absorption spectrum is shown in Fig. 2, and it will be observed that it is slightly more absorptive than glyceryl  $\alpha\beta$ -dinitrate.

Glyceryl  $\alpha$ - and  $\beta$ -mononitrates were prepared by extracting the neutralised, concentrated mother liquors left after the extraction of the dinitrates, as described by Will (*loc. cit.*).

The absorption spectra of glyceryl  $\alpha$ - and  $\beta$ -mononitrates in aqueous solution are shown in Fig. 3. The  $\alpha$ -compound prepared

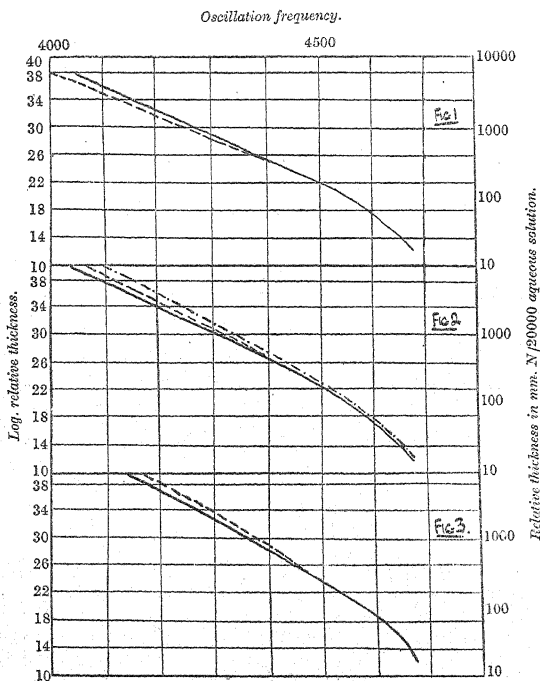


FIG. 1.—Nitroglycerin { ————— Labile or stable form.  
 - - - - - Commercial nitroglycerin.

FIG. 2.— {  $\alpha$ -Methylin dinitrate —————  
 Glyceryl  $\alpha\beta$ -dinitrate - - - - -  
 Glyceryl  $\alpha\gamma$ -dinitrate - . . . .

FIG. 3.— { Glyceryl  $\alpha$ -mononitrate —————  
 Glyceryl  $\beta$ -mononitrate - - - - -

by Nef's method gave a spectrum almost identical with that prepared by the direct nitration of glycerol. It will be observed that

both isomerides exhibit less absorption than either the isomeric dinitrates or the trinitrate, and that the unsymmetrical  $\alpha$ -isomeride is rather more absorptive than the symmetrical  $\beta$ -isomeride.

The absorption spectrum of glycerol does not appear to have been investigated, and a sample of Hehner's glycerol, used as the standard in the chemical analysis of glycerol used for dynamite, and guaranteed to contain no impurity except water, was examined after drying over phosphoric oxide in a vacuum for four days. It was found that a normal aqueous solution was quite diactinic through a thickness of 10 mm.

It is therefore evident that the substitution of a hydrogen atom of one of the hydroxyl groups of glycerol by a nitro-group produces a profound change in the absorption spectrum, whereas the substitution of one or both hydrogen atoms of the remaining hydroxyl groups by nitro-groups, whilst increasing the general absorption, does not produce nearly so great a change in the absorption spectrum.

#### EXPERIMENTAL.

##### *Preparation of Pure Nitroglycerin (Glyceryl Trinitrate).*

One hundred and eighty grams of Prices's double distilled glycerol were nitrated with a clear, mixed acid of the composition:

	Per cent.
Nitric acid .....	40.0
Sulphuric acid .....	57.68
Nitrous acid .....	0.18
Water .....	2.14

The nitration was carried out in a large beaker surrounded by a freezing mixture, the glycerol being added at such a rate as to keep the temperature at 10—12° throughout the nitration. The ratio of acid to glycerol was about 7:1. Air stirring was continued for ten minutes after the whole of the glycerol had been added, after which the nitroglycerin was allowed to separate for thirty minutes, no accelerant being employed.

The lower layer of mixed acid was then run off, and the nitroglycerin washed with twelve successive changes of distilled water at 25—30°, the addition of sodium carbonate or any other stabilising substance being avoided. The nitroglycerin was then successively fractionated five times in a freezing mixture. The last fraction, of about 100 grams, was dried in a vacuum over solid potassium hydroxide, and finally obtained as a clear, mobile, faint yellow oil which, after solidification, melted at 13.1°. (Found: N=18.49. Calc.: N=18.51 per cent. H<sub>2</sub>O=nil.)

*Isolation of the Labile and Stable Forms of Nitroglycerin.*—The method adopted for the isolation of the labile and stable forms of nitroglycerin was similar to that described by Hibbert (*loc. cit.*). The labile form was isolated by inoculating nitroglycerin cooled to  $-40^{\circ}$  with a trace of the labile form obtained by cooling two to three drops of nitroglycerin mixed with glass wool to  $-40^{\circ}$ , and stirring vigorously. The operation had to be repeated three times before the labile form was obtained, but this was probably due to the fact that the nitroglycerin had been previously frozen. This form appeared to crystallise in the triclinic system, and melted at  $2.0^{\circ}$ .

The stable form was readily isolated by allowing the nitroglycerin to freeze slowly without inoculation. Large bipyramidal crystals were obtained which melted at  $13.1^{\circ}$ .

Both forms were allowed to liquefy in a vacuum desiccator over solid potassium hydroxide, and used at once for the spectrographic examination. For the confirmation of the spectrographic results, fresh samples of the labile and stable solid forms were prepared and recrystallised before use.

*Commercial Nitroglycerin.*—This product had been made by nitrating glycerol (for dynamite) with commercial mixed acid almost identical in composition with that previously described. A trace of hydrocarbon oil had been used to accelerate the separation, and the nitroglycerin had been stabilised by thoroughly washing with dilute sodium carbonate solution followed by several washings with water at  $30^{\circ}$ . The sample was filtered twice and dried over solid potassium hydroxide in a vacuum desiccator for forty-eight hours. It possessed a distinct brown colour, melted at  $12.5^{\circ}$ , and contained  $N=18.46$  per cent. (measured by the nitrometer).

The material was used in this condition for the investigation of the absorption spectrum.

*$\alpha$ -Methylin Dinitrate.*—This was fractionally crystallised three times and dried in a vacuum over solid potassium hydroxide. The sample examined spectrographically crystallised in white, monoclinic prisms melting at  $24.2^{\circ}$ , and contained  $N=14.23$  per cent.

*Preparation of the Lower Nitrates of Glycerol.*—The method adopted for the preparation of the lower nitrates of glycerol was on similar lines to that described by Will (*loc. cit.*). Two hundred grams of glycerol were nitrated with a clear, mixed acid of the composition:

	Per cent.
Nitric acid .....	21.76
Nitrous acid .....	0.06
Sulphuric acid .....	68.22
Water .....	9.96

The nitration was conducted exactly as described under the preparation of trinitroglycerin. On allowing the mixture to remain, about 50 grams of nitroglycerin were separated, after which the mixed acid containing the lower nitrates and a little nitroglycerin was diluted and repeatedly extracted with ether after removing a little nitroglycerin which separated on dilution.

The crude dinitrates were twice washed with a little water, filtered, and partly dried. The  $\alpha\beta$ - and  $\alpha\gamma$ -dinitrates were separated as described by Will (*loc. cit.*), except that glass wool was used in place of kieselguhr.

The crude  $\alpha\gamma$ -dinitrate was purified by repeated fractional crystallisation, and about 30 grams were finally obtained in large, water-white, prismatic crystals which melted at  $26^\circ$ . On desiccating over calcium chloride in a vacuum for three days, a pale yellow oil was obtained containing N=15.30 per cent., and this was identical with the "dinitroglycerin K" described by Will.

The crude  $\alpha\beta$ -dinitrate showed no tendency to crystallise when cooled at  $-20^\circ$  overnight, but, on inoculation, a little  $\alpha\gamma$ -dinitrate separated. This was repeated until no further traces of the  $\alpha\gamma$ -dinitrate separated, after which it was dried over calcium chloride in a vacuum. The  $\alpha\beta$ -dinitrate was obtained in this way as a dark yellow oil containing N=15.22 (Calc.: N=15.38 per cent.).

Both dinitrates were kept in a vacuum over solid potassium hydroxide until the solutions were made up for spectrographic examination.

The mononitric esters of glycerol were obtained by evaporating the neutralised mother liquors left after the extraction of the dinitrates, as described by Will (*loc. cit.*). The crude mixture of  $\alpha$ - and  $\beta$ -nitrates was easily crystallised by cooling to  $-20^\circ$  and vigorously rubbing with a glass rod. Traces of dinitrate were removed from this crude product by dissolving in water and extracting with ether. The separation of the two nitrates was effected by repeatedly washing with a little ether cooled to  $-20^\circ$ , when it was found that the  $\beta$ -mononitrate was rather more readily soluble than the  $\alpha$ -isomeride.

Both forms were obtained in fine leaflets which, after recrystallising twice from water, gave the following results on analysis:

	M. p.	Found N <sub>2</sub> per cent.	Theoretical.
$\alpha$ -Mononitrate.....	$57^\circ$	10.2	10.2
$\beta$ -Mononitrate.....	$54^\circ$	10.13	

*Glyceryl  $\alpha$ -Mononitrate prepared from Epichlorohydrin.*—A sample of the  $\alpha$ -mononitrate was prepared from epichlorohydrin, as described by Nef (*Annalen*, 1904, 335, 238). It was found that



the conversion of epichlorohydrin into epi-iodohydrin, and the latter into glycide nitrate, proceeded quite normally.

Fifty grams of glycide nitrate were heated at  $100^{\circ}$  with 40 grams of water for four hours. The product was dried in a vacuum over sulphuric acid, and the crude product melted at  $54^{\circ}$ . It was purified by recrystallisation from ether, this process being repeated three times, when 40 grams of glyceryl  $\alpha$ -mononitrate were obtained. The product melted at  $57.5^{\circ}$  and crystallised in small, white prisms. When mixed with an equal quantity of the  $\alpha$ -mononitrate, prepared by the direct nitration of glycerol, the mixture melted at  $58^{\circ}$ .

Unsuccessful attempts were made to prepare the  $\alpha$ -mononitrate by the direct nitration of glycide, as described by Hanriot (*Ann. Chim. Phys.*, 1879, [v], 17, 118), but only a very small yield of the  $\alpha$ -mononitrate was obtained.

*Spectrographic Examination.*—The instrument used was a Hilger quartz spectrograph, size C, fitted with a wave-length scale. The iron arc was used as the source of illumination, and the wave-length scale was standardised against the zinc and copper arcs.

All observations were conducted in aqueous solution, the water employed being diactinic up to 2100 Å.U.

### Summary.

From an examination of the absorption spectrum of glycerol and its nitric esters, it is evident that:

(1) The labile and stable forms of nitroglycerin are physical isomerides, and both forms are identical in aqueous solution.

(2) Commercial nitroglycerin is more absorptive than pure nitroglycerin.

(3) The order of increasing absorption in aqueous solution is  $\beta$ -mononitrate,  $\alpha$ -mononitrate,  $\alpha\gamma$ -dinitrate,  $\alpha\beta$ -dinitrate, and trinitrate.

(4)  $\alpha$ -Methylin dinitrate is rather more absorptive than glycerol  $\alpha\beta$ -dinitrate.

(5) The displacement of a hydrogen atom of one of the hydroxyl groups of glycerol by a nitro-group produces a much more profound change in the absorption spectrum than the displacement of one or both hydrogen atoms of the remaining hydroxyl groups.

(6) There does not appear to be any numerical proportionality between the number of hydrogen atoms of the hydroxyl groups displaced by nitro-groups and the degree of absorption for any particular dilution.

The author is indebted to Mr. P. A. Baldock, M.Sc., for confirmation of some of the results described in this paper, and also to the Research Committee of Messrs. Nobel's Explosives Co., and particularly to Messrs. Rintoul and Cowie, for the facilities accorded to him for the carrying out and publication of this work.

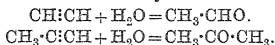
ARDEER.

[Received, May 26th, 1919.]

## LXIX.—*The Interaction of Acetylene and Mercuric Chloride.*

By DAVID LEONARD CHAPMAN and WILLIAM JOB JENKINS.

ALMOST forty years ago, M. Kutscheroff (*Ber.*, 1881, **14**, 1532, 1540) made the important discovery that hydrocarbons of the acetylene series unite with water in the presence of mercury salts being thereby converted into aldehydes and ketones.



As is well known, the reaction is of special importance, since it is now employed on a commercial scale for the preparation of acetaldehyde, which is subsequently converted by oxidation into acetic acid.

The mechanism of the action of acetylene on mercury salts in the presence of water and aqueous solutions of acids has been studied by Keiser (*Amer. Chem. J.*, 1893, **15**, 537), K. A. Hofmann (*Ber.*, 1898, **31**, 2217; 1899, **32**, 870; 1904, **37**, 4459), Biltz and Mumm (*Ber.*, 1904, **37**, 4417), Biltz (*Ber.*, 1905, **38**, 133), Biginelli (*Ann. Chimica*, 1898, 16), and Brame (*T.*, 1905, **87**, 427).

Keiser, Hofmann, and Biltz and Mumm investigated the white precipitate obtained by passing acetylene into an aqueous solution of mercuric chloride. Keiser assigned to this substance the formula  $\text{ClHg}\cdot\text{C}:\text{C}\cdot\text{HgCl}$ , which is probably not correct. Hofmann considers that the first product to be formed is a substance having

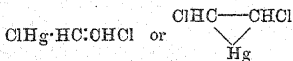
the constitutional formula. 
$$\begin{array}{c} (\text{ClHg})_2\text{C} \text{---} \text{CCl}_2 \\ \diagdown \quad \diagup \\ \text{Hg} \end{array}$$
, this being rapidly

hydrolysed to trichloromercuriacetaldehyde,  $(\text{ClHg})_3\text{C}\cdot\text{CHO}$ . Biltz and Mumm have shown that the white precipitate almost certainly has the constitution of trichloromercuriacetaldehyde, but they regard the evidence for the formation of the intermediate compound assumed by Hofmann as unsatisfactory.

Brame has pointed out that both Hofmann and Biltz failed to notice that Biginelli had observed the formation of small quantities of another substance having the constitution  $\text{ClHg}\cdot\text{HC}:\text{CHCl}$ . By the action of acetylene on a solution of mercuric chloride in dilute hydrochloric acid, Brame has prepared the compound in crystalline form and in sufficient quantity to demonstrate some of its properties. He concludes that there seems good reason for believing that the first action of acetylene on either aqueous or dilute acid solutions of mercuric chloride is the formation of the compound  $\text{ClHg}\cdot\text{HC}:\text{CHCl}$  by direct addition, together with acetaldehyde. He adds, however, that it remains to be proved whether this additive compound is an intermediate product concerned in the production of acetaldehyde or whether it is a secondary substance derived from the aldehyde.

The chief product of the action of acetylene on a solution of mercuric chloride in dilute hydrochloric acid is acetaldehyde, and it is therefore unlikely that Biginelli and Brame succeeded in converting more than a small proportion of the acetylene into the additive compound of mercuric chloride and acetylene, and it was no doubt chiefly for this reason that Brame was loth to conclude that it was an intermediate compound concerned in the production of acetaldehyde. His reluctance to draw this conclusion may also have been due to his observation that although the crystals were only sparingly soluble in water, they did not begin to separate from the mercuric chloride solution until the acetylene had been acting on the latter for several hours.

We have recently discovered a method whereby a large proportion of the mercuric chloride can be converted into a crystalline compound of the composition  $\text{HgCl}_2\cdot\text{C}_2\text{H}_2$ . From 72 grams of mercuric chloride, 50 grams of the additive compound were obtained. Unlike the other mercury compounds obtained by the action of acetylene on the salts of mercury, it is dissolved by most organic solvents. In ether or benzene it is very readily soluble, and can be purified by crystallisation from either of these solvents. It is also unique in having a low melting point. In this respect it resembles the mercury alkyl and mercury alkyl haloid compounds, a circumstance that lends support to the view that the constitutional formula of the compound is either



The acetylene was prepared from calcium carbide, and was collected in two gas-holders of 18 litres capacity. The gas was

circulated for eighteen hours through a saturated solution of mercuric chloride in absolute alcohol (72 grams of mercuric chloride in 75 c.c. of absolute alcohol) through which a slow current of dry hydrogen chloride had been passed for five minutes. After sixteen hours, long, colourless, needle-shaped crystals were deposited in the solution. At the end of the experiment these were collected by the aid of the pump. The mass of the crystals was 10 grams. On pouring the solution into a large volume of water, 40 grams of a white solid were precipitated. This was soluble in ether or benzene; it was crystallised from the latter solvent, and proved to be the same substance as the crystals which had separated from the alcoholic solution during the experiment.

An analysis of the product furnished the following results:

Found: C=7.93; H=0.693; Cl=23.67. Hg=68.76.

$C_2H_2.HgCl_2$  requires C=8.07; H=0.677; Cl=23.83; Hg=67.42 per cent.

Owing to decomposition, the melting point could not be accurately determined. It was in the neighbourhood of  $113^\circ$ .

An attempt was made to prepare the compound by passing acetylene through an ethereal solution of mercuric chloride in which dry hydrogen chloride had been dissolved. The acetylene was circulated for twenty hours. At the end of the experiment, the ether was distilled off from the resulting solution, and the solid residue examined. It was almost completely soluble in water, and practically none of it was dissolved in benzene. Therefore the solid residue was almost entirely unchanged mercuric chloride, and very little, if any, of the additive compound could have been formed. It seems likely, therefore, that the compound  $HgCl_2.C_2H_2$  is only produced when acetylene is passed into solutions of mercuric chloride in ionising solvents, the compound being formed by the direct addition of the ions  $HgCl^+$  and  $Cl^-$  to the unsaturated hydrocarbon.

From the above experiments, it seems probable that the first product of the interaction of acetylene and mercuric chloride is a compound having the constitutional formula  $ClHg \cdot HC \cdot CHCl$ . The most interesting property of the compound is its solubility in dry organic liquids, for this circumstance, and the fact that excellent yields of it can now be obtained, suggest that it may prove to be a useful reagent in organic synthesis.

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LXX.—*The Basic Properties of Phenanthraquinone.*

By JOSEPH KNOX and HELEN REID WILL.

THE investigation of the basic properties of phenanthraquinone was undertaken as part of a scheme for the investigation of the basic properties of oxygen in organic compounds in general. The results in the case of organic acids and phenols are given in a paper by Knox and Richards (this vol., p. 508), which contains also references to the earlier literature on the subject.

The method adopted was to determine the solubility of the organic compound in water and in solutions of mineral acids of increasing concentration. Increasing solubility of the organic compound with increasing concentration of the acid solution is taken to indicate salt-formation in solution. The salt-formation is assumed to be due to the formation of compounds of the oxonium type by the passage of the oxygen from the bivalent to the quadri-valent condition, as explained in the previous communication (*loc. cit.*).

A red, crystalline nitrate of phenanthraquinone is described by Kehrman and Mattisson (*Ber.*, 1902, 35, 343), who ascribe to it

the constitution  $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{O} < \begin{array}{l} \text{H} \\ \text{O} \cdot \text{NO}_2 \end{array} \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{O} \end{array}$ . They also obtained a red,

crystalline compound of phenanthraquinone with sulphuric acid, which, however, was not analysed. They assume that the dark green solution obtained when phenanthraquinone is dissolved in concentrated sulphuric acid contains a salt in which each oxygen atom of the phenanthraquinone is combined with a molecule of sulphuric acid, whilst the red, crystalline compound is regarded as analogous to the nitrate.

In the present investigation, the solubility of phenanthraquinone in water and in various concentrations of sulphuric, hydrochloric, and nitric acids has been determined at 25°. In order that the solubility determinations in the various acids should be comparable, the following method was chosen. A weighed quantity of pure, powdered phenanthraquinone was placed in a glass-stoppered flask and 200 c.c. of the acid solution were added. The flask was allowed to remain in the thermostat at 25° for several days, with frequent shaking, until the solution was saturated. Each concentration of acid was shaken with phenanthraquinone for varying periods until constant results were obtained. The undissolved phenanthraquinone was then rapidly filtered through a tared Gooch crucible,

washed with cold water until free from acid, dried at  $100^{\circ}$ , and weighed. The solubility in water was determined by shaking at  $25^{\circ}$  until saturated and evaporating a litre of the saturated solution to dryness on the water-bath and weighing. The following are the results of the solubility determinations. The concentration of the acid solution is given in gram-equivalents per litre and of the phenanthraquinone in grams per litre.

*Solubility of Phenanthraquinone in Sulphuric Acid at  $25^{\circ}$ .*

Conc. $\text{H}_2\text{SO}_4$ .....	0.00	5.97	6.19	7.00	9.48	11.6	13.7
Conc. $\text{C}_{14}\text{H}_8\text{O}_2$ ...	0.0075	0.0080	0.0085	0.0095	0.012	0.019	0.030
Conc. $\text{H}_2\text{SO}_4$ .....		15.1	17.1	18.6			
Conc. $\text{C}_{14}\text{H}_8\text{O}_2$ ...		0.043	0.082	0.116			

*Solubility of Phenanthraquinone in Hydrochloric Acid at  $25^{\circ}$ .*

Conc. $\text{HCl}$ .....	0.00	3.11	4.25	5.12	6.05	6.07	7.20
Conc. $\text{C}_{14}\text{H}_8\text{O}_2$ ...	0.0075	0.012	0.016	0.023	0.029	0.031	0.046
Conc. $\text{HCl}$ .....		8.50	9.25	10.8			
Conc. $\text{C}_{14}\text{H}_8\text{O}_2$ ...		0.058	0.088	0.157			

*Solubility of Phenanthraquinone in Nitric Acid at  $25^{\circ}$ .*

Conc. $\text{HNO}_3$ .....	0.00	4.26	4.54	5.02	6.15	6.66	6.70
Conc. $\text{C}_{14}\text{H}_8\text{O}_2$ ...	0.0075	0.049	0.053	0.067	0.099	0.114	0.118
Conc. $\text{HNO}_3$ .....		7.20	7.45	8.30			
Conc. $\text{C}_{14}\text{H}_8\text{O}_2$ ...		0.157	0.175	0.227			

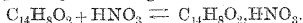
These results are shown graphically in the diagram, in which the ordinates represent the concentration of the phenanthraquinone in centigrams per litre and the abscissæ the concentration of the acid in gram-equivalents per litre.

A high degree of accuracy is not claimed for these solubility determinations. They are, however, sufficiently accurate to show that in every case the solubility increases with increasing concentration of the acid, indicating that phenanthraquinone has basic properties. For the reasons given by Knox and Richards (*loc. cit.*), these basic properties are attributed to the formation of salts of the oxonium type, in which the oxygen becomes quadrivalent.

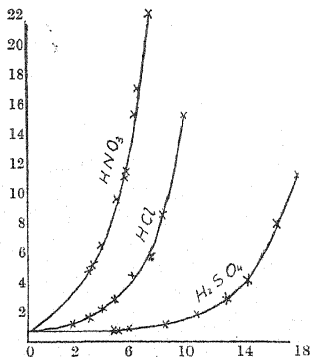
The increase in solubility is greatest in nitric acid and least in sulphuric acid for equivalent concentrations. This was also found to be the case with organic acids and phenols (*loc. cit.*), so that salt-formation occurs most readily with nitric acid and least readily with sulphuric acid.

An attempt was made to determine the concentration of nitric

acid which is in equilibrium with phenanthraquinone and the nitrate,  $C_{14}H_8O_2 \cdot HNO_3$ , according to the reversible reaction



The equilibrium is reached very slowly, however, from the left-hand side. By shaking phenanthraquinone at  $25^\circ$  with various concentrations of nitric acid, it was found that the red nitrate was formed with concentrations of acid in the neighbourhood of  $12.5N$ , but that slightly more dilute acid acted very slowly, as indicated by the very slow fall in concentration of the acid with continued shaking. Even with  $12.5N$ -acid, the concentration of the acid diminished only slightly, although the red compound was obviously present, since the nitrate is formed on the surface of the phen-



anthraquinone and prevents further action of the acid. The equilibrium was therefore approached from the other side. The red nitrate was prepared by the method described by Kehrman and Mattisson, and shaken at  $25^\circ$  with various concentrations of nitric acid. When the concentration of nitric acid was below  $11.2N$ , decomposition of the nitrate took place comparatively rapidly until the concentration of the nitric acid rose to this value, provided that sufficient nitrate was added to have both solid phases, phenanthraquinone and its nitrate, present at equilibrium. At  $25^\circ$ , therefore, phenanthraquinone and its nitrate,  $C_{14}H_8O_2 \cdot HNO_3$ , are in equilibrium with  $11.2N$ -nitric acid.

# LXXI.—The Solubility of Silver Acetate in Acetic Acid and of Silver Propionate in Propionic Acid.

By JOSEPH KNOX and HELEN REID WILL.

THE solubility of silver acetate was determined at 25° in water and in various concentrations of acetic acid, up to about 17*N*, in order to see whether an acid salt was formed under these conditions. In the analogous case of sodium acetate and acetic acid, two acid salts,  $C_2H_3O_2Na, C_2H_4O_2$  and  $C_2H_3O_2Na, 2C_2H_4O_2$ , are formed (Farmer, T., 1903, **83**, 1440; Vasilieff, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 753; Dukelski, *Zeitsch. anorg. Chem.*, 1909, **62**, 114; Abe, *Mem. Coll. Sci. Eng. Kyōtō*, 1911, **3**, 13; Dunningham, T., 1912, **101**, 431). In the case of silver acetate and acetic acid at 25°, the solubility curve is continuous, indicating that no new phase is formed. The solubility of silver propionate in various concentrations of propionic acid was also determined, and a continuous solubility curve also obtained.

The silver salts were purified by recrystallisation from water, and shown by analysis to be pure. Excess of the salt was shaken with water or varying concentrations of the corresponding acid until constant solubility was obtained. The silver salt in solution was determined gravimetrically as silver chloride, and the acid by titration with sodium hydroxide free from carbonate. The experimental results are as follows. The concentration of the silver salt is given in grams per litre, and that of the acid in gram-equivalents per litre.

## Solubility of Silver Acetate in Acetic Acid Solutions at 25°.

Conc. $C_2H_3O_2Ag$ .	11.13	10.73	10.32	9.98	9.52	9.19	8.72	8.29	7.73	7.31
Conc. $C_2H_4O_2$ ...	0.00	1.00	2.00	2.98	4.19	4.98	5.99	6.80	8.01	8.97
Conc. $C_2H_3O_2Ag$ .	6.78	6.15	5.33	4.96	4.29	3.43	2.48	1.09		
Conc. $C_2H_4O_2$ ...	9.96	11.02	12.32	12.97	13.97	14.96	15.93	17.28		

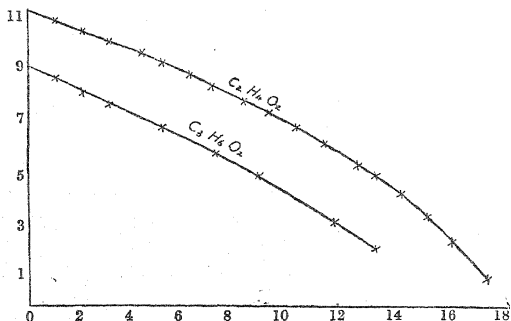
## Solubility of Silver Propionate in Propionic Acid Solutions at 25°.

Conc. $C_2H_3O_2Ag$ .	9.04	8.58	8.01	7.60	6.78	5.78	4.96	3.16	2.17
Conc. $C_2H_6O_2$ ...	0.00	1.00	2.00	2.97	4.95	6.97	8.56	11.40	13.03



The results of the solubility determinations are shown graphically in the diagram, in which the ordinates represent the concentration of the silver salt in grams per litre and the abscissæ the concentration of the acid in gram-equivalents per litre.

The solubility of silver acetate in water at 25° is given by Goldschmidt (*Zeitsch. physikal. Chem.*, 1898, **25**, 91) as 11.18 grams per litre, and by Jaques (*Trans. Faraday Soc.*, 1909, **5**, 225) as 11.07 grams per litre. The value obtained by interpolation from



Raupenstrauch's results at 20° and 30°, recalculated to grams per litre, is 11.21 grams (*Monatsh.*, 1885, **6**, 585). For silver propionate in water at 25°, Goldschmidt (*loc. cit.*) gives 9.04 grams per litre, and the same figure is obtained from Raupenstrauch's results (*loc. cit.*). These values for the solubility of silver acetate and silver propionate in water at 25° agree closely with ours.

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[Received, June 16th, 1919.]

*Emission Spectra and Atomic Structure.*

A LECTURE DELIVERED BEFORE THE CHEMICAL SOCIETY ON  
MARCH 6TH, 1919.

By JOHN WILLIAM NICHOLSON.

THE invitation of the Council of the Chemical Society to take part in a series of three lectures during the present session is peculiarly acceptable to me, in that it gives me an opportunity to draw attention to certain problems of atomic structure in which further progress can scarcely be hoped for without a more complete co-operation between the physicist and chemist than has hitherto been customary.

The chemist appeals frequently to the physicist, or even to the mathematician, for guidance. I wish to emphasise, and I hope that my remarks will serve to do so, that it is even more a necessity that the real aid to be invoked in the problem which we share in common—that of the elucidation of the nature of the elementary atom—is that of the chemist. It is my belief that this problem will not proceed further towards a satisfactory solution without the joint action of the physicist and the chemist, who have hitherto tended to work in separate channels, without a complete knowledge of their mutual activities. Some of the problems in which co-operation is desirable I hope to indicate, perhaps vaguely, but sufficiently clearly for those of us who have really common interests.

Prof. Soddy has relieved my task very much. One of the pioneers on the chemical side, he gave an account of the bearing of chemistry on the problem of atomic structure which is beyond criticism, and to which nothing further can really be added from that point of view. Some questions were raised on which more could perhaps be said—for instance, the spectra of isotopes, to which I may refer again. As regards his address, I should like to say at the outset that the views therein expressed cannot be contested seriously by the physicist or the mathematician who has worked at the problem of atomic structure.

My own object is to consider this problem from the point of view of spectra. I will endeavour to confine my remarks to the more immediate issues, for the subject of spectra is at present so vast as to transcend any delimitation as a branch of chemistry or of physics. I must consider it only from the point of view of atomic structure, which I have already described as the ultimate aim of both physics and chemistry, an aim only to be achieved by

co-operative effort, and preferably by the existence at the same time of strong chemical and physical schools at one of our leading universities. Prof. Soddy began at the "heavy" end of the periodic table of the elements. I shall, in effect, begin at the "light" end—with hydrogen and helium and possible lighter elements. Before I so begin, however, a few words regarding the nature of spectra are necessary—and my remarks are confined to emission spectra, and not absorption spectra, which, although of supreme importance to the chemist, are less interesting as bearing on the structure of the atom.

Any complete account of the nature of spectral series, as elucidated by experiment, would be quite outside the limits of time of a single lecture. I must perforce neglect various matters, such as satellites of spectrum lines, as of secondary importance. The account of spectra which I give must be accepted as an ideal simplification of existing spectra, to which, nevertheless, theories of atomic structure must conform. Moreover, it is not to be understood that such an account is valid for the heavier elements, the spectra of which exhibit a more complex scheme of relations, but since atomic theories must in practice be illustrated or even confirmed from the lighter and more chemically simple elements, showing the simpler types of spectra, no disadvantage is thereby involved.

Series of spectrum lines will then be regarded as falling into three mutually related sets—the so-called diffuse, sharp, and principal series. The existence of any one of these implies that of the other two, and the lines constituting any one of these series may be single, double, or triple. An element may emit two distinct sets of series, perhaps more. For instance, helium gives three series of single lines and three of doublets. It is a great advantage to work with wave numbers, or numbers of complete wave-lengths in a centimetre, rather than wave-lengths themselves, in the discussion of series, for this procedure enables the relations of the three types of series to be stated very simply. If we proceed along a spectrum series towards the violet, the lines are seen to become closer and closer together until a limit is reached at which two successive members coincide. Lines are never, in fact, visible in the laboratory near this limit, although their convergence towards it can be seen readily enough, the actual limit being a matter of calculation. The diffuse and sharp series tend to the same limit in all cases, and from this limit we can calculate, and thereby predict, the wave-number intervals between the lines of the principal series. The Rydberg-Schuster law gives also the limit of the principal series.

In regard to double lines, the series relations are even more interesting. The wave-number interval between the two members of a doublet is constant along the diffuse and sharp series—the two members form separate series tending to different limits. In a principal series, on the other hand, they tend to the same limit, and the doublets rapidly become narrower towards the violet end of the spectrum.

Our present interest in these questions is mainly confined to the discovery of a chemical atom which can produce a set of ethereal waves the frequencies of which are related in this curious manner.

I will endeavour to summarise some of the more extreme difficulties met at the outset. In the first place, a series contains an infinite number of lines, and if the spectra are in any sense dynamical vibrations of the atom, the frequencies of which are transmitted to our instruments by the ether, the atom must have an infinite number of degrees of freedom. This is not consistent with the very finite number of possible vibrating parts which, from many converging lines of evidence, we are now compelled to assume for its structure—the positive nucleus and some electrons in rotation round it. The only way to surmount this difficulty is, in fact, to postulate that series spectra are derived from the nucleus, and are not a question of the outer electrons. This nucleus must then be endowed with an extremely complex structure. In this way, we might hope to preserve the conception of spectra as dynamical vibrations, and all the lines of the three series might then arise simultaneously from the same atom. We cannot altogether reject this possibility, but if it were more than a possibility, we should be driven to a very disappointing conclusion. For nuclear structure is a thing we may, and often do, speculate about, but it is at the same time practically beyond the power of our experiments. We know, for instance, that  $\alpha$ - and  $\beta$ -particles in radioactive phenomena are shot from the nucleus, but nothing we can do appears to have any retarding or accelerating effect on such phenomena or to give a clue to the arrangement of the particles before their emission. We cannot, in fact, influence the nucleus in any effective way, but only its surrounding electrons. Speculative theories of spectra as arising from a nucleus may then be constructed in the future, but there would remain the fundamental difficulty of testing them experimentally. Many phenomena, however, for instance, the Zeeman and Stark effects, and the curious variations shown in the spectra of mixed gases, seem to indicate that the surrounding electrons are vitally concerned and that the nucleus gives us no mode of escape.

Since we cannot have the infinite number of degrees of freedom,

the conception of an infinite number of states of an atom arises with a finite number of spectrum lines—perhaps only one—corresponding with each state. Two lines of the same series are then never given simultaneously from the same atom. This underlies the two theories of production of spectra which have achieved some success, namely, the theories of Ritz and Bohr, on which more will be said later.

The second difficulty to which I shall refer is that all the formulæ which give a useful expression for the series relations of spectral lines serve to show quite conclusively that the frequencies of the lines are simple functions of a quantity to which we can assign any whole-number value we please, each value corresponding with a definite line. Dynamical theory always leads to an expression for the *square* of the frequency, and the frequency itself is a square root which ordinarily does not work out into a simple form. This difficulty is of a type which I do not wish to expound at length now, but it is sufficient to say that a satisfactory theory of spectra as atomic vibrations must lead to an equation giving the frequency itself, and not its square, in the first instance. There is only one known case in which this occurs, namely, the case in which the forces which regulate the vibrations of the atomic electrons are mainly *magnetic*. This is the manner in which Ritz overcomes the difficulty. He found it necessary to postulate the existence of a specific magnetic moment—the *magneton*, in fact—which was invariable, like the electric charge of an electron, from atom to atom. An atom could contain various numbers of magnetons, each corresponding with one of its “states,” and each state gave a spectrum line when the electrons of the atom vibrated under the influence of the elementary contained magnets.

This theory of spectra was extraordinarily successful. Its prophecies were verified at every turn, and it was the instrument which, more than any other, has directed the experimental work of spectroscopists into fruitful channels and led to a consolidation of the phenomena of spectra into great generalisations which are now fully established. It led, in fact, to the well-known *combination principle* of spectra on which Bohr's theory was subsequently founded. The defects which are regarded as fatal to it are derived from other considerations than those of spectra. Such problems as the scattering of  $\alpha$ - and  $\beta$ -particles by atoms, treated experimentally and compared with the theory developed by Darwin, Bohr, and others, do not appear to be consistent with such fields of magnetic type, although Hicks has had some success in the contrary direction in interpreting the deflections of these particles by a magnetic core of the atom.

I do not propose to say more regarding the existence of magnetic forces within the atom or as regards the existence or non-existence of the magneton itself. There is a vast amount of literature on the subject, which only, in fact, comes into the scope of existing theories of spectra in the manner already briefly indicated. The other theory which has had some success in explaining series spectra is of quite another type, and does not admit such magnetic forces. We shall discuss it later, but shall proceed at present to consider some spectra which do not form ordinary series.

It is difficult to think of an atom as a nucleus of positive electricity with satellite electrons without imagining that the atom is capable of vibrations of a periodic type, and that these vibrations must show themselves in the form of optical wave-lengths. These should, from general considerations, have a frequency which brings many at least into the visible spectrum. The argument is founded merely on the accepted—from many well-established facts—values of the radii, electronic velocities, and so forth. I will proceed to give a short account of some of my own work in this connexion, the data on which it is founded being mainly those of spectroscopic astronomy.

In the first place, one very general result must be stated. It is so frequently ignored in the construction of theoretical atoms that too much emphasis can scarcely be given. Under the inverse square law of attraction or repulsion of elements of electricity, or, indeed, any inverse law at all, coplanar rings of electrons are not possible, in the sense that even an undisturbed atom cannot preserve its configuration. The conclusion may probably be extended to non-coplanar rings.

Rutherford has shown that the nucleus apparently continues to act on electrons with this law at distances less than the atomic radius, and there is much evidence that the electrons continue so to act on each other. If this is confirmed further, the explanations of the phenomena of Röntgen radiation, based on transfer of an electron from one ring to another, will fall to the ground. The subject has many ramifications, and the following statements, capable of logical demonstration, show the chaos in which the physics of the atom is now involved:—

(1) Experiments on scattering of  $\alpha$ - and  $\beta$ -particles by atoms indicate that the usual laws of electrical action are valid *inside* the atom. This precludes comparable forces of magnetic origin.

(2) Separate rings of electrons are impossible if (1) is true, and this would annihilate attempts hitherto made to interpret the characteristic X-radiation of atoms, which then can only be a property of the nucleus.

(3) The now accepted dimensions of this nucleus are not consistent with (2). They are also not consistent with the fact that it is capable of sending out  $\beta$ -particles during a radioactive change, for a single  $\beta$ -particle is much larger than a nucleus.

It would be possible to continue such a table of contradictions for a considerable time, and if the quantum theory is invoked, the situation is little better. I do not wish to do more than indicate the position, for more could not be done in a sufficient space. What I wish to make clear is that whilst those who, like Prof. Soddy, discuss radioactive phenomena, proceed from the "heavy" end of the periodic table, any constructive account of spectra must begin at the "light" end.

For the simplest possible elements, there can only be a question of one ring, whatever view is adopted. My own procedure was as follows. Taking the ordinary laws of electrical action, it is possible to work out the frequencies of dynamical vibration of an atom with, say, any number of electrons up to six, in one ring, rotating round a nucleus of any defined strength. The ratios of these frequencies are pure numbers in most cases, although for certain defined vibrations there is a small correction involving the ratio of mass of the electron and nucleus. We may search for vibrations, falling into groups with the prescribed ratios among individual members, in any spectrum that is known to emanate from matter of the simplest form—determined by the fact that no known element heavier than helium, for instance, is indicated as being present—and if such a spectrum is found which falls completely into such groups there is an a priori case for the conclusion that we have given a theory of the spectrum which is satisfactory, and of necessity settles many points of atomic structure.

The nebulae and the solar corona have been generally believed to consist of the simplest forms of matter. They have always been invoked by speculators on the periodic table and its possible "early" elements, and with much reason. The spectrum of a nebula, for instance, contains only lines of hydrogen and helium, and others which cannot be produced in the laboratory after every possible mode of deriving them from likely elements has been tried. The spectrum of the corona, whilst rich in lines, contains nothing that can be produced in the laboratory. Naturally, in a search for the groups in specified numerical ratios, derived from precisely described atoms, we began with these spectra. The results were startling. The coronal spectrum consists entirely of lines—in number about thirty-six—which all fit precisely into the scheme of ratios for elementary atoms in which the nucleus has a charge  $5e$  or  $7e$ , and five or seven electrons rotating round it, as the case

may be, in its normal state, and smaller or greater numbers in its charged states. The chemical identity of the atom must be regarded as determined by the charge of its nucleus—or its atomic number. The whole coronal spectrum can thus be linked up as the superposed spectra of two chemical substances, and represented by simple formulæ. It was found, moreover, that these formulæ would go further and predict the existence of new and unobserved spectrum lines. A notable instance was the coronium line  $\lambda 6374$  found by MM. Deslandres and Carrasco some time after the publication of the formula which predicted it, and similar predictions in the case of the spectra of planetary nebulæ have been verified. The corresponding substances in the nebulæ which are invoked as hypothetical entities are the same in kind as those for the solar corona, differing only in nuclear charge or atomic number. It is curious to note that the atomic numbers of the necessary hypothetical atoms for nebulæ are the even numbers 2, 4, 6, and for the corona they are odd numbers, 5, 7. The coronal spectrum appears to come in the main from these hypothetical atoms endowed with strong negative charges, for instance, the atom  $7e$  with 9 revolving electrons. This points to an abundance of negative electrons in the corona, unattached to atoms and readily capable of attachment. There is much evidence, at the same time, that the atoms themselves are endowed with very high velocities, and may be a new form of  $\alpha$ -particle.

To return to our main argument. What all these atoms share in common is the fact that their angular momenta are simple multiples of a constant unit. Armed with this generalisation, we can calculate the spectrum of any of these hypothetical elements—say one in the nebulæ—from that of another of different chemical nature—say one in the corona. I ventured to put forward the suggestion that this was the real basis of the quantum theory, and that the angular momenta of the electrons in all atoms were related in this simple way to a universal constant of nature, which, being an angular momentum, had the proper dimensions, and even the proper numerical value, as calculation showed, of Planck's unit.

Dr. Bohr, in the theory of series spectra which he subsequently put forward, adopted this generalisation. Prof. Jeans is to address you on the subject the fringe of which we are now touching, so that I will proceed no further, but turn aside to another aspect of importance to chemists. We have seen already that in certain spectrum lines calculated in the way outlined above, there will be a small discrepancy of wave-length due to the fact that the nucleus itself oscillates, as well as the electrons, in the types of vibration producing these lines. Its mass must therefore enter into the



question in these special cases, and it enters as a small term of order  $m/M$ , where  $m$  is the mass of the electron and  $M$  that of the nucleus. From the discrepancies, we can calculate  $M/m$ , which, with our practical knowledge of  $H/m$ , where  $H$  is the mass of the hydrogen atom, gives us  $M/H$ , the *atomic weight* of the hypothetical atom. Very concordant results are obtained from these calculations. The atomic weight of coronium, the name given to the hypothetical atom causing the most striking line  $\lambda 5303$  in the coronal spectrum, is 4.0, suggesting that it may be a helium atom radiating in an unusual manner in an unusual environment; but the atomic weight of the other element there required is 2.0, which corresponds with no known terrestrial element. Again, in the nebulae, the two most important atoms required give atomic weights 1.3, 3.0, again with no known terrestrial equivalent. Yet, nevertheless, MM. Buisson and Fabry, by their method of determining the mass of a radiating atom from the interference of its radiation, experimentally confirmed the value 3.0, and showed that the element for which our value is 1.3 had an atomic weight greater than, but not much greater than, that of hydrogen. It seems necessary to presume the existence, in circumstances which we perhaps are unable to produce at present in the laboratory—and maintain for a length of time—of such atoms which may not be chemical elements in the sense ordinarily understood by that term.

We have, in fact, two alternatives. Either the atoms in question have not an existence or have not been produced terrestrially, or we have not yet excited them in the laboratory in the appropriate manner to produce such spectra. The latter alternative seems more probable. There is reason to believe that the coronal spectrum at least consists of a somewhat scattered "negative band" spectrum, produced in the presence of an excess of electrons by a very mild form of excitation. However that may be, these spectra, although without doubt the first spectra to receive a strict theoretical basis which is satisfactory, are not *series* spectra as known to us, being in the nature of their relations very analogous to, and without doubt a special case of, band spectra. Series spectra themselves, as defined above, cannot, as we have seen, be ascribed to dynamical vibrations about an atomic condition of steady motion.

Before we proceed to series spectra, we should perhaps state the assumptions involved in the above work. They are, in effect, identical with the conclusions derived by Sir Ernest Rutherford on experimental grounds about six months after the publication of the first paper in which some of these results were obtained. In fact, they can all be included in the statement that the nucleus is at least as small as an electron, and that the law of force between

electric charges is *strictly*—to an extreme order of approximation—that of the inverse square. It is not necessary at this point to emphasise the very definite atomic structure which these results imply. The law of inverse square, the small nucleus, the existence of Planck's constant as a universal angular momentum, are simple examples of what can be deduced. The law of at least some negative spectra of atoms, previously unknown, is another corollary. Many of these deductions have been confirmed by the later experimental work, on quite other ground, of Rutherford and of his colleagues, and have to a large extent become part of the essential basis of Bohr's theory of spectra and its extraordinary consequences, recently worked out by Paschen and others, in regard to the fine structure of lines in the spectrum of hydrogen.

The spectra which we have just described are not series spectra in the ordinary sense of the term. They are in all essentials band spectra. Their production in the laboratory from known materials involves a new type of experiment—an experiment in which a gas of extreme tenuity must be excited by an electric force insufficient to ionise the gas and thus detach an electron, but sufficient to show a “dynamical vibration” spectrum after an exposure of many hours. No such form of excitation has yet been tried in any experimental production of spectra, but it is now being tried by Dr. Merton. It appears to be the only hope of producing some of these elusive astronomical spectra in the laboratory, and thus reaching one of the goals of the astronomical spectroscopist.

It is already clear that series spectra cannot be “dynamical vibration” spectra from the reasons cited above. What are they? The only suggestion which has met with any considerable success is that of Dr. Bohr. Proceeding from the point of view outlined above, he supposes, for instance, that an atom of hydrogen can have one electron rotating with an angular momentum which is any multiple of  $h/2\pi$ , where  $h$  is Planck's constant. He calculates the energy in any such state of rotation—a *stationary* state—and assumes that radiation is emitted in the passage between two such stationary states of amount equal to the loss of energy between the states, and also of amount  $h\nu$ , where, in accordance with Planck's law,  $\nu$  is the frequency of the emitted vibration. He thus deduces the hydrogen spectrum as containing the frequencies

$$\nu = B\left(\frac{1}{m^2} - \frac{1}{n^2}\right),$$

where  $m$  and  $n$  are any integers and  $B$  is a universal constant dependent on Planck's constant, the calculated value of which approximates in a remarkable way to Rydberg's universal constant of spectra. The theory does, in fact, reproduce the hydrogen

spectrum, although, of course, that of Ritz, founded on the magneton, did the same, and is too frequently ignored. I wish at this point to make a remark which seems to me essential, and relates to a matter not previously dealt with effectively by theoretical physicists intent upon constructing models of a hydrogen atom which can give the Balmer series spectrum. This spectrum consists of about six lines in the laboratory. The actual spectrum of the hydrogen *atom* contains more than a thousand lines, the rest being the so-called "secondary spectrum." At least six theories of a hydrogen atom have now been given, leading to the Balmer series as its spectrum. But none gives any clue to the origin of the secondary spectrum of hydrogen, which is the real key to the problem of atomic structure, for it is known to be due in the main to the hydrogen *atom*, and not the molecule. I regard the disentanglement of this spectrum into its component bands and series as the most fundamental problem of modern spectroscopy. It is the great simplicity of the formula for the Balmer series which renders it so easy to construct physical theories to account for it. These theories are, nevertheless, unable to carry conviction if they do not provide for a much more extensive spectrum of the hydrogen atom, and no theory has yet even begun this task, which is one of great difficulty in the case of an atom believed to contain only one electron.

I have naturally confined my attention mainly to the more fundamental matters which relate to the simplest chemical atoms. Time is too short to enter into many other interesting points, such, for instance, as the fine structure of the hydrogen lines, which Dr. Merton and I have been elucidating recently. It is now known, for instance, that the Balmer series is a principal series, and not a diffuse series, as hitherto assumed. This result alone has an important bearing on the mechanism of production of this series from an assigned atom. If we were to discuss the spectra of mixed gases or of molecules, a host of problems remains to be solved, and can only be solved by co-operation of the physicist and chemist. To give only one instance, we may ask a question. In a mixture of calcium and barium molecules, with perhaps a temporary association  $\text{CaBa}$ , what relation would the spectrum of such a molecule have to those of the calcium and barium molecules? The whole question of the spectra of the temporary associations found in vacuum tubes, and analysed by Sir J. J. Thomson's method of "positive rays," remains for solution. All such work will bear on the problem of atomic structure, for an atom is not satisfactory unless it also forms molecules the spectra of which are deducible from that of the atom. No present model of a hydrogen atom appears as yet to have succeeded.

*The Quantum Theory and New Theories of  
Atomic Structure.*

A LECTURE DELIVERED BEFORE THE CHEMICAL SOCIETY ON  
MAY 1ST, 1919.

By JAMES HOPWOOD JEANS.

THE problem of the structure of matter falls into two parts: first, the problem of determining the constituent parts of matter, and, second, that of determining the laws according to which these constituent parts move and react with one another.

It has for some time been universally accepted that the fundamental constituents of matter are electrical in their nature, consisting of bodies of infinitesimal size carrying electric charges which are inseparable from them. Briefly speaking, matter is made up of positive and negative charges of electricity. The properties of the bodies carrying the negative charges are fairly well known. These bodies are the negative electrons; they all carry precisely the same charge and have precisely the same mass. They are independent of the chemical nature of the substance to which they belong, and so form standardised and interchangeable parts of all atoms. The same electron which at one instant forms part of an atom of hydrogen may at some future instant form part of an atom of iron; at another instant it may play the rôle of a "free" electron, its motion contributing to the carrying of an electric current through a mass of metal or of gas.

The properties of the positive charges, or "nuclei" as they are commonly called, are known with less certainty. I will try to discuss these properties in their logical order rather than in the chronological order of their discovery. Rutherford has proved that the  $\alpha$ -rays emitted by radioactive substances are positively charged particles; he has shown that they all carry the same charge, and that this is equal, numerically, to twice the charge carried by a negative electron. If  $-e$  is the charge carried by each negative electron, the  $\alpha$ -particle carries a charge  $+2e$ . Thus an  $\alpha$ -particle and two negative electrons would form a system carrying zero charge—an electrically neutral system. The system constituted in this way has been shown by Rutherford to be the normal helium atom. Thus the positive nucleus of the helium atom is simply the  $\alpha$ -particle; its charge is  $+2e$ ; its mass is, of

course, the mass of the helium atom minus twice the mass of a negative electron. Since the mass of the helium atom is about 7300 times that of a negative electron, we may say that the positive nucleus carries practically all the mass of the helium atom.

The size of the negative electron is well known. The variation of its mass with its velocity proves that the whole of its mass is electromagnetic, and this circumstance enables us to assign to it the definite radius  $2 \times 10^{-13}$  cm. The size of the helium atom is also known—from the kinetic theory of gases. Its radius is almost exactly  $10^{-8}$  cm., or just about 50,000 times that of the negative electron.

We are led to wonder whether the positive nucleus carries most of the "size" of the atom as well as most of its mass. The answer is provided by experiments on the scattering of  $\alpha$ -particles by matter. Imagine a jet of  $\alpha$ -particles directed on to a thin sheet of matter. If the  $\alpha$ -particles were of the size of helium atoms, it is clear that they would be obstructed at every point by the atoms of the matter, and would not emerge as a jet at all. It has, in point of fact, been found that the majority of the  $\alpha$ -particles emerge with their paths only slightly deflected by their encounters with the atoms of the matter, whilst a few have their paths deflected through quite large angles. The inference which must be drawn is that not only are the  $\alpha$ -particles excessively minute, but also that the parts of the atoms which are effective in deflecting the paths of the  $\alpha$ -particles are themselves excessively minute. The actual amount of scattering observed agrees quantitatively with this conclusion, provided it is assumed that each atom contains only one positive nucleus, its size being infinitesimal compared with the size of an atom, and its charge being approximately proportional to the atomic weight of the matter.

Thus the normal atom is found to consist of a certain number,  $N$ , of negative electrons, each of charge  $-e$ , and a positive nucleus of extremely minute size and of charge  $Ne$ . For helium we have already seen that  $N=2$ , and the question immediately arises as to the value of  $N$  for other elements.

This problem has been solved by experiments on the X-ray spectra of the elements. Suppose the elements are arranged in order of their atomic weight, beginning with hydrogen, the lightest, leaving unoccupied gaps where the periodic law suggests that an element remains to be discovered, for example, between tungsten and osmium, and reversing the order of elements where this is demanded by the periodic law, so that, for instance, cobalt is placed before nickel and argon before potassium. The "atomic number"  $N$  of any element is that which represents its position in

this series. Thus for hydrogen  $N=1$ , for helium  $N=2$ , for lithium  $N=3$ , for argon  $N=18$ , for potassium  $N=19$ , for silver  $N=47$ , and so on. Then Moseley and others have proved—and I think most physicists are content to accept the proof as conclusive—that the number of negative electrons in the normal uncharged atom of any element is equal to the atomic number  $N$  of that element. The charge on the positive nucleus of an atom of an element is accordingly  $Ne$ , where  $N$  is the atomic number of the element.

This settles, I think, in the opinion of most physicists, finally and incontrovertibly, the problem of determining the ingredients of the atom. The uncharged hydrogen atom consists of a single negative electron of charge  $-e$  and a positive nucleus of charge  $+e$ , the mass of which is something like 1840 times that of the negative electron. The uncharged helium atom consists of two negative electrons and a nucleus of charge  $2e$ , and so on.

The problem of determining how these constituents are arranged and move inside the atom is still far from complete solution. The material we have to work on consists almost entirely of the spectra of the elements; these provide a mass of data which admit of accurate measurement to five, or even six, significant figures. Knowing the structure of, say, the hydrogen atom, we could calculate its spectrum if we knew its laws of motion, just as Newton, conjecturally knowing the law of gravitation, could calculate what the orbit of a planet ought to be.

Suppose, for instance, that the positive nucleus and the negative electron, which form the normal hydrogen atom, moved according to the ordinary electrostatic law, by which the force varies as the inverse square of the distance. The positive nucleus, being 1840 times more massive than the negative electron, would remain practically at rest, whilst the electron would describe an elliptical orbit about it. The radiation which would be emitted by an electron describing such an orbit can readily be calculated. There would be orbits of all possible sizes, and therefore of all possible periods, so that the emitted radiation would be of all possible frequencies—in other words, the spectrum would be continuous. Since the spectrum of the hydrogen atom consists of sharply defined lines, it is therefore at once clear that the motion in the hydrogen atom is not governed by the ordinary electrostatic laws. Precisely similar reasoning shows that the electron cannot move under any continuous force from the positive nucleus.

Knowing the laws of motion, we could determine the spectrum. Unfortunately, the converse problem is not soluble; knowing the spectrum, we cannot deduce the laws of motion. Some knowledge of a general kind can be obtained—in particular, the laws of motion

are necessarily discontinuous, for continuous laws of motion would lead to a continuous spectrum.

So far, we have considered the atomic spectrum. A somewhat similar situation presents itself when we turn to the consideration of the continuous spectrum of a solid. Except for irregularities arising from imperfect emission of the surface, all solid bodies give the same spectrum at the same temperature. The nature of this spectrum depends on the laws which govern the motion of the electrons by which the radiation is emitted. Different spectra would correspond with different laws of motion, and conversely. Again, if we knew the laws of motion, it would be possible to determine the spectrum.

If the motion of the electrons were governed by the classical laws of mechanics (Newton's laws), it can be shown that the spectrum would be of a very special type—there would be no wave-length of maximum energy, but the energy would increase indefinitely as the wave-length decreased. Thus the total spectral energy at any finite temperature would be infinite, all the energy running into the waves of shortest wave-length. It is therefore clear that the motion of electrons is not governed by the classical laws of mechanics.

In 1901 Planck, starting from a system of laws which differed entirely from the classical laws, and in particular involved the idea of discontinuous motion, arrived at a spectral formula which has since been found to agree extremely well, probably perfectly, with the observed spectrum of a solid. Although Planck's spectral formula, regarded as an expression of a fact of nature, has since gained universal acceptance, his method of deducing it has been widely objected to, mainly on account of his assumption of discontinuous motion. In 1910 I was able to show that Planck's formula could not possibly be arrived at except from a system of laws which involved discontinuities of some kind, and, further, I found that the nature of these discontinuities must necessarily be substantially of the type already assumed by Planck. Almost identical conclusions were enunciated by Poincaré about a year later, together with important additions.

Thus from a study of the continuous spectrum of a solid we conclude that the motion of the radiation-emitting electrons must be of a discontinuous nature. It is, unfortunately, not possible to specify the nature of these discontinuities completely, but a good deal is known. When the electron is executing isochronous vibrations, the total energy of the vibration (potential plus kinetic) must fall into "quanta." The energy may be equal to one quantum, two quanta, etc., but cannot involve fractions of the quantum. Thus

when the energy changes, there must be an instantaneous absorption or emission of a whole quantum of energy. In general, however, when the energy of a vibration changes, the frequency also changes. Now the "quantum" of energy is not the same for all vibrations; it depends on the frequency of the vibration. If  $\nu$  is the frequency, the quantum is  $h\nu$ , where  $h$  is a universal constant of nature—Planck's "Wirkungsquantum." Thus if an electron jumps from a vibration in which it has  $n_1$  quanta, its frequency being  $\nu_1$ , to a vibration in which it has  $n_2$  quanta, its frequency being  $\nu_2$ , it must instantaneously emit an amount of energy  $h(n_1\nu_1 - n_2\nu_2)$ .

Evidence as to what happens to the energy thus suddenly emitted is provided by the photoelectric phenomenon. To ionise an atom of any substance requires an amount of energy,  $Q$ , which depends on the nature of the atom. Now the atoms of any substance can be ionised by light, but only by light the frequency of which is above a critical value  $\nu_0$ , which again depends on the nature of the atom. This frequency  $\nu_0$  is related to the energy  $Q$  required for ionisation by the relation  $Q = h\nu_0$  (approximately at least). Thus it looks as though light of frequency  $\nu$  travelled through the ether tied up in some way in bundles of amount  $h\nu$ —in fact, in quanta. This is Einstein's hypothesis of light-quanta; no doubt it does not express the whole truth, but it must be somewhere near to the truth.

Accepting this hypothesis provisionally, the amount of energy,  $h(n_1\nu_1 - n_2\nu_2)$ , which we imagined to be set free from one atom, will wander through space as a single quantum; in order that it may satisfy the quantum relation (energy =  $h\nu$ ), its frequency must be  $n_1\nu_1 - n_2\nu_2$ .

On these foundations, Bohr has, with extraordinary skill and acumen, developed his theory of line-spectra. The frequency  $\nu_1$  of the original vibration having  $n_1$  quanta must depend on  $n_1$ , and similarly  $\nu_2$  must depend on  $n_2$ . Thus the frequency of the emitted vibration will be expressible mathematically in a formula of the type

$$f_1(n_1) - f_2(n_2),$$

and on giving all possible values to  $n_1$  and  $n_2$ , we ought to obtain the whole line-spectrum of the element.

The case of the hydrogen atom is particularly simple. To a first approximation we may consider the massive positive charge as being at rest, and the formula is found to be

$$N\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right).$$



This gives exactly the hydrogen spectrum (Balmer's series being given by  $n_1=2$ , Lyman's series by  $n_1=1$ , etc.) provided  $N$  is equal to Rydberg's constant. Now the theoretical value of  $N$  depends only on universal constants of nature. The value of each of these is known to about 1 part in 200, and on inserting these values, the theoretical value of  $N$  is found to be equal to Rydberg's constant to about 1 part in 200. There is thus the most brilliant agreement, both quantitatively and qualitatively, between the observed spectrum of hydrogen and the theoretical spectrum predicted by Bohr's theory.

The assumption that the massive positive nucleus stands at rest is only approximately true; actually it will oscillate round the centre of gravity of itself and the negative electron, and this will introduce a correction of the order of  $M/m$ , the ratio of the mass of the nucleus to that of the electron. By comparing the theoretical correction with spectroscopic observations, Fowler has deduced for  $M/m$  the value 1835, a value which agrees exceedingly well with other determinations of  $M$  and  $m$ .

Still one other correction of a most fascinating kind must be mentioned. Bohr's theory takes its simplest form when the electron orbits are assumed to be circular; the simple spectral laws are exact for circular orbits. Consistently with the quantum dynamics, however, the electron can also describe a series of elliptic orbits. This possibility gives rise to a new series of frequencies which differ only from those of circular orbits by quantities of the order of  $(v/V)^2$ , where  $V$  is the velocity of light and  $v$  that of the electron in its orbit. The theory of relativity makes it possible to calculate the corrections to the frequencies introduced by the ellipticities of the orbits. Sommerfeld has carried the calculation through, and believes that the whole series of frequencies exactly account for the fine structure of the spectral lines. The agreement, so far, is limited to the single line  $H_\alpha$ ; for this, it is perfect both qualitatively and quantitatively, and I venture to predict that a similar explanation will soon be found of the fine structure of other lines.

This is as far as we can go with any confidence. It seems to me that experimental evidence and abstract reasoning combined practically limit us to one view of the structure and mechanism of the simpler atoms, and this view is confirmed by a large amount of exact spectroscopic evidence. The structure is that of the so-called Rutherford atom; the simpler atoms (hydrogen and helium at least) consist of an extremely minute central nucleus with one or more negative electrons revolving round. The mechanism is

that of Bohr's theory, and is based upon, and governed by, the quantum dynamics.

We cannot, I think, claim to know anything with certainty as to the ultimate structure of the more complex atoms, especially those of radioactive substances, and our definite knowledge of atomic mechanism is practically limited to the few cases in which the atom contains only two constituents—the hydrogen atom, the positively charged helium atom, and possibly also the doubly-charged lithium atom. The "problem of three bodies" has not yet been solved in quantum dynamics any more than in gravitational theory. This is scarcely surprising in view of the fact that the whole quantum theory is wholly a creation of the present century.

We cannot speak with any confidence as to the mechanism of complete molecules other than the monatomic helium molecule; for even the simplest complete molecule, the hydrogen molecule, consists of four constituent parts. If progress continues at its present rate, however, there is every reason for hoping that within a few years the whole scheme of quantum-mechanics will have been unravelled. The problems of valency, stereochemistry, the periodic law, the stability of chemical compounds, their optical and colour properties, and a host of other chemical problems, will then become the province of the mathematician. In spite of the rapidly progressing fusion of all branches of science, the chemist and the mathematician have up to the present remained almost independent. It seems possible that in the near future the chemist will scarcely think of making progress except with the help of the mathematician. In spite of its history of extraordinary triumphs, chemistry is to-day as much an empirical science as electricity was before the time of Maxwell. If once chemistry becomes a mathematical science, it may progress at a rate at present undreamed of.

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## LXXII.—*Interaction of Mercuric and Cupric Chlorides Respectively and the Mercaptans and Potential Mercaptans.*

By PRAFULLA CHANDRA RAY.

SOME four years ago, the author ventured to put forth the view that the compounds which mercuric, platinic, and cupric chlorides, respectively, yield with thiocarbamide and thioacetamide, etc., are of the same nature as those obtained by the interaction of these

haloids and real mercaptans, that is, they are chloromercaptides (P., 1914, 30, 304), and it seemed desirable to undertake a systematic study of the behaviour of mercuric, cupric, and platinic chlorides towards some of the typical mono- and di-mercaptans, namely, ethyl and ethylene mercaptans (dithioethylene glycol) and 2-thiol-5-thio-4-phenyl-4:5-dihydro-1:3:4-thiodiazole.

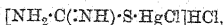
Ethyl mercaptan yields under normal conditions chloroplatinum mercaptide,  $(\text{EtS})_2\text{PtCl}$ , and under exceptional conditions platinous mercaptide,  $(\text{EtS})_2\text{Pt}$ . Dithioethylene glycol also yields a chloromercaptide of the formula  $\text{C}_2\text{H}_4\langle\text{S}\rangle\text{PtCl}\cdot\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{SH}$ . In the

formation of this remarkable compound, two molecules of dithioethylene glycol simultaneously take part in the reaction; one atom of chlorine of the platinic chloride remains, however, intact.

The potassium salt of 2-thiol-5-thio-4-phenyl-4:5-dihydro-1:3:4-thiodiazole has been found to be equally reactive towards platinic chloride, and it readily yields mercaptides in which platinum functions both as a triad and a dyad element, as in the case of the simple ethyl mercaptan.

The valency of platinum calls for a few remarks. The salts of the type  $\text{MX}_3$  are scarcely represented among the platinum compounds. In the formula  $(\text{EtS})_2\text{PtCl}$ , no doubt platinum may be made to appear as quadrivalent by doubling it. Platinum has its proper place in the eighth or transitional group in the periodic system, which also includes iron and iridium. Now, the chlorides of these metals are represented by the simple formula  $\text{MCl}_3$ , and not by  $\text{M}_2\text{Cl}_6$ . Moreover, platinum, with the high atomic weight of 194, will scarcely permit of the coalescence of two atoms into the complex  $:\text{Pt}\cdot\text{Pt}:$ . Salts containing two atoms of platinum in the molecule have no doubt been described, but they are of a very complex character (Cossa, *Ber.*, 1890, 23, 2503; Cleve, *Bull. Soc. chim.*, 1872, 17, 289).

The product of the reaction of mercuric chloride with thiocarbamide has been assigned the formula  $\text{HgCl}_2\cdot\text{CSN}_2\text{H}_4$  (Rosenheim and Meyer, *Zeitsch. anorg. Chem.*, 1903, 34, 62; 1906, 49, 13). In other words, it has been regarded as a mere additive or molecular compound. From considerations based on analogy, the author suggested that it should be formulated as



that is, that it is the product of the reaction of mercuric chloride on  $\psi$ -thiocarbamide. The hydrogen chloride which is formed is not liberated in the free state, but is simply fixed by the basic complex. It is well known that formamidine disulphide exists as a salt of a diacidic base, because of the presence of two amino- and

imino-groups. Convincing proof has recently been obtained in support of the above formula. The compound in question has been found to be sufficiently soluble in water to admit of conductivity measurements. If it were an additive one, it would dissociate into its components on dissolution. Now, thiocarbamide is practically a non-electrolyte, and mercuric chloride is very feebly ionised in solution (compare Rây and Dhar, T., 1913, 103, 8).

The aqueous solution, however, shows an enormous increase in the dissociation, which is of the same order as that of ammonium chloride, proving that the salt is the hydrochloride of a base.

Thiocarbamide may be expected to behave in like manner towards platinic chloride and yield a compound of the same type, thus:  $2\text{CS}(\text{NH}_2)_2 \xrightarrow{\text{PtCl}_4} [(\text{NH}_2\cdot\text{C}(\cdot\text{NH})\cdot\text{S})_2\text{PtCl}_2]\text{HCl}$ . Both Reynolds and Prätorius-Seidler (compare Rathke, *Ber.*, 1884, 17, 307), however, regard the compound as an additive one of thiocarbamide with platinous chloride, and assign to it the formula  $(\text{CSN}_2\text{H}_4)_2\text{PtCl}_2\cdot\text{HCl}$  or  $(\text{CSN}_2\text{H}_4)_2\text{PtHCl}_3$ . That this view is erroneous is evident from another consideration. The platinic chloride on being reduced to the platinous state would set free chlorine, which would in turn act on a portion of the thiocarbamide, and formamidine disulphide hydrochloride would be simultaneously formed;\* the derivative in question is, however, free from it.

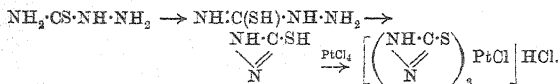
Cupric chloride is analogous in its behaviour towards thiocarbamide,  $\text{CS}(\text{NH}_2)_2 \xrightarrow{\text{CuCl}_2} \text{NH}_2\cdot\text{C}(\cdot\text{NH})\cdot\text{S}\cdot\text{CuCl}$ . In this case, however, the hydrogen chloride is liberated in the free state and can be detected in the filtrate. This is what might have been expected. The chlorides of mercury, platinum, and cobalt are capable of forming complex compounds with ammonia, amines, and amino-groups, which, on account of their basic character, can fix a molecule of hydrogen chloride, whilst copper, being a more positive metal, does not possess this property.

The view taken above offers also a ready interpretation of the reaction between platinic chloride and thioacetamide, first studied by Kurnakov (*J. Russ. Phys. Chem. Soc.*, 1893, 25, 613), who formulates the compound as  $\text{PtCl}_2\cdot 4\text{C}_2\text{H}_5\text{NS}\cdot\text{PtCl}_4$ , that is, as an additive one of four molecules of thioacetamide with one of platinous chloride and another of platinic chloride. This formula, when halved, stands as  $\text{PtCl}_3\cdot 2\text{C}_2\text{H}_5\text{NS}\cdot\text{HCl}$ , and is in reality  $[(\text{CH}_3\cdot\text{C}(\cdot\text{NH})\cdot\text{S})_2\text{PtCl}_2]\text{HCl}$ , the platinic chloride functioning

\* It has been actually found that sulphuryl dichloride, which acts as a mild chlorinating agent, behaves exactly like iodine towards thiocarbamide and yields the hydrochloride of the base.

exactly like mercuric chloride. Thioacetamide here also simply undergoes tautomeric change. One strong argument in favour of the suggested constitution is afforded by the fact that if platonic chloride were actually to be reduced to the platinous form, the available atoms of chlorine would act on two other molecules of thioacetamide. It has already been shown that iodine completely decomposes thioacetamide, the whole of the sulphur being precipitated (T., 1916, 109, 698). The product in question when treated with carbon disulphide, however, did not yield any sulphur. The corresponding cupric chloride derivative has been found to conform to the formula  $\text{CH}_3\cdot\text{C}(\text{NH})\cdot\text{S}\cdot\text{CuCl}$ ; it is, in fact, a chloromercaptide.

The reaction between platonic chloride and thiosemicarbazide is of special interest. The compound obtained has the formula  $\text{C}_3\text{H}_4\text{N}_6\text{Cl}_2\text{S}_3\text{Pt}$ . Here also a tautomeric change of the thio-compound evidently takes place under the influence of the haloid, resulting in the formation of a cyclic compound with the elimination of a molecule of ammonia, thus:



The mercaptan now acts on platonic chloride in the usual manner, the product being a chloromercaptide. Of the three molecules of hydrogen chloride generated, one is fixed by the complex substance because of its basic character, due to the presence of several imino-residues.

#### EXPERIMENTAL.

##### *Mercaptans and Metallic Haloids.*

*Ethyl Mercaptan and Platonic Chloride.*—Hofmann and Rabe (*Zeitsch. anorg. Chem.*, 1897, 14, 294) state that if to chloroplatinic acid is added ethyl mercaptan in alcoholic solution, at first an orange-yellow platonic mercaptide,  $(\text{EtS})_4\text{Pt}$ , is formed which, when heated to  $100^\circ$  in a vacuum, readily yields platinous mercaptide. It has been found, however, that by the interaction of platonic chloride and ethyl mercaptan, chloroplatinum mercaptide,  $(\text{EtS})_2\text{PtCl}$ , is almost invariably formed, and that it is only under exceptional conditions that platinous mercaptide,  $(\text{EtS})_2\text{Pt}$ , can be obtained. The method is therefore given here somewhat in detail. To a concentrated alcoholic solution of chloroplatinic acid is added a very dilute alcoholic solution of ethyl mercaptan from time to time with vigorous shaking; for the first

few moments, only a deep orange coloration is noticed, but shortly after an orange-yellow precipitate begins to appear. Care should be taken that the platinic chloride is always in sufficient excess. If the conditions of reaction are reversed, that is, if a dilute solution of platinic chloride is added in small quantities at a time to an excess of a concentrated alcoholic solution of ethyl mercaptan with vigorous shaking, for a few minutes the solution remains clear, after which a yellow salt begins to separate, which is very nearly pure platinous mercaptide.

*Chloroplatinum mercaptide:*

I. 0.050 gave 0.0276 Pt, 0.022 AgCl, and 0.065 BaSO<sub>4</sub>.  
Pt=55.2; Cl=11.33; S=17.85.

II. 0.0502 gave 0.0283 Pt and 0.0675 BaSO<sub>4</sub>. Pt=56.37;  
S=18.47.

III. 0.0226 gave 0.0126 Pt. Pt=55.75.

IV. 0.0191 gave 0.0081 AgCl and 0.0242 BaSO<sub>4</sub>. Cl=10.51;  
S=17.44.

C<sub>4</sub>H<sub>10</sub>ClS<sub>2</sub>Pt requires Pt=55.02; Cl=10.09; S=18.19 per cent.

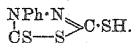
*Platinous mercaptide:*

0.1317 gave 0.0814 Pt, 0.012 AgCl, and 0.1985 BaSO<sub>4</sub>.  
Pt=61.81; Cl=2.25; S=20.71.

C<sub>4</sub>H<sub>10</sub>S<sub>2</sub>Pt requires Pt=61.43; S=20.24 per cent.

Contamination with distinct traces of the previous compound, which is invariably formed, accounts for the presence of chlorine.

*2-Thiol-5-thio-4-phenyl-4:5-dihydro-1:3:4-thiodiazole,*



*and Platinic Chloride.*—To a concentrated aqueous solution of the potassium salt was added, with stirring, a dilute solution of chloroplatinic acid in a thin stream. A yellow precipitate was obtained which, on drying, became orange. Here also, as in the case of ethyl mercaptan, the platinum atom functions as trivalent and bivalent:

0.080 gave 0.0213 Pt and 0.1805 BaSO<sub>4</sub>. Pt=26.63; S=31.00.

A second preparation gave Pt=25.32.

(C<sub>8</sub>H<sub>5</sub>N<sub>2</sub>S<sub>3</sub>)<sub>3</sub>Pt requires Pt=22.33; S=33.14.

(C<sub>8</sub>H<sub>5</sub>N<sub>2</sub>S<sub>3</sub>)<sub>2</sub>Pt requires Pt=30.12; S=29.18.

Mean: Pt=26.23; S=31.16 per cent.

It will thus be seen that here also a compound containing quadri-

\* The estimation throughout was effected by fusion with sodium nitrate and sodium carbonate.

valent platinum is never formed, but a mixture of almost equal proportions of the compounds containing tervalent and bivalent platinum.

In the above reactions, the free hydrogen chloride of chloroplatinic acid, acting on a portion of the potassium mercaptide, liberates the corresponding mercaptan, which is insoluble in water, and the available chlorine atoms of the quadrivalent platinum chloride also acting on the potassium mercaptide give rise to the disulphide, which is equally insoluble. The dried precipitate was therefore exhausted first with alcohol and afterwards with benzene in order to extract impurities. The colour of the compound changed from yellow to orange under this treatment.

#### *Dimercaptans and Metallic Haloids.*

*Dithioethylene Glycol and Platinic Chloride.*—A dilute alcoholic solution of platinic chloride was gradually added, with vigorous stirring, to a concentrated alcoholic solution of dithioethylene glycol. A yellowish-brown precipitate was obtained, which was washed with alcohol and dried in a vacuum. It conforms to the

formula  $C_2H_4 \begin{smallmatrix} S \\ \diagup \diagdown \\ S \end{smallmatrix} PtCl \cdot S \cdot C_2H_4 \cdot SH$ :

0.0788 gave 0.0373 Pt, 0.032 AgCl, and 0.1608 BaSO<sub>4</sub>.

Pt=47.34; Cl=10.05; S=28.03.

$C_4H_8ClS_4Pt$  requires Pt=46.96; Cl=8.58; S=30.93 per cent.

There is reason to conclude that a simpler mercaptide of the formula  $C_2H_4 \begin{smallmatrix} S \\ \diagup \diagdown \\ S \end{smallmatrix} PtCl_2$  (Pt=54.39; Cl=19.88; S=17.91) is simultaneously formed in small quantities; the higher results for platinum and chlorine and the lower result for sulphur are thus accounted for. Attempts to obtain the chloromercaptide in a purer form proved unsuccessful.

#### *Potential Mercaptans and Metallic Haloids.*

*Thiocarbamide and Mercuric Chloride.*—The components interacted both in alcoholic and in aqueous solution; a copious white precipitate was obtained, which was washed with alcohol and dried in a vacuum. The filtrate was neutral. (Found: C=3.82; H=1.63; N=8.14; Cl=20.45; S=10.03; Hg=56.62.  $CH_3N_2Cl_2SHg$  requires C=3.46; H=1.18; N=8.07; Cl=20.46; S=9.22; Hg=57.64 per cent.)

*Conductivity Measurement.*

V.	T.	$\mu$ .
256	21.5	98.96

There were evidently two ions in solution, and the dissociation is of the order of that of ammonium chloride.

*Thiocarbamide and Platinic Chloride.*—An acetone solution of thiocarbamide was cautiously added, with constant stirring, to platinic chloride solution. An orange-yellow precipitate was obtained, which was washed with alcohol and dried in a vacuum:

I. 0.0838 gave 0.0365 Pt, 0.0910 BaSO<sub>4</sub>, and 0.0804 AgCl.  
Pt=43.56; S=14.91; Cl=23.74.

0.0582 gave 6.6 c.c. N<sub>2</sub> at 33° and 760 mm. N=12.39.

II. 0.0496 gave 0.0540 BaSO<sub>4</sub> and 0.0482 AgCl. S=14.95;  
Cl=24.03.

C<sub>3</sub>H<sub>7</sub>N<sub>4</sub>Cl<sub>3</sub>S<sub>2</sub>Pt requires Pt=43.01; S=14.17; Cl=23.57;  
N=12.40 per cent.

*Thiocarbamide and Cupric Chloride.*—To an alcoholic solution of cupric chloride was added, with constant stirring, an alcoholic solution of the carbamide. The granular precipitate when dried in a vacuum was white with a faintly blue tint:

0.0608 gave 0.0275 CuO. Cu=36.09.

0.0443 „ 6.2 c.c. N<sub>2</sub> at 31° and 760 mm. N=15.41.

0.0588 „ 0.0483 AgCl and 0.0780 BaSO<sub>4</sub>. Cl=20.31;  
S=18.22.

CH<sub>3</sub>N<sub>2</sub>ClSCu requires Cu=36.38; N=16.12; Cl=20.44; S=18.43  
per cent.

*Thioacetamide and Platinic Chloride.*—Thioacetamide in alcoholic solution was added, with stirring, to platinic chloride solution, and the brownish-yellow precipitate was treated as before:

I. 0.0852 gave 0.0360 Pt; 0.0782 AgCl. Pt=42.26;  
Cl=22.79.

II. 0.0334 gave 0.0144 Pt. Pt=43.11.

0.0813 „ 5.2 c.c. N<sub>2</sub> at 32° and 760 mm. N=7.01.

III. 0.1457 gave 0.0630 Pt, 0.1697 BaSO<sub>4</sub>, and 0.1313 AgCl.  
Pt=43.83; S=15.99; Cl=22.29.

C<sub>4</sub>H<sub>9</sub>N<sub>2</sub>Cl<sub>3</sub>S<sub>2</sub>Pt requires Pt=43.20; S=14.23; Cl=23.68;  
N=6.23 per cent.

*Thioacetamide and Cupric Chloride.*—The method of preparation was exactly the same as in the preceding case, the salt being almost white. The alcoholic filtrate, when distilled off, was found to contain free hydrogen chloride:



I. 0.0555 gave 0.0250 CuO. Cu=35.95.

0.0595 „ 4.6 c.c. N<sub>2</sub> at 29.5° and 760 mm. N=8.57.

II. 0.2818 „ 0.1261 CuO, 0.42 BaSO<sub>4</sub>, and 0.2250 AgCl.  
Cu=35.78; S=20.44; Cl=19.75.

C<sub>2</sub>H<sub>4</sub>NCISCu requires Cu=36.59; S=18.53; Cl=20.55; N=8.11  
per cent.

*Thiosemicarbazide and Platinic Chloride.*—A dilute solution of platinic chloride was added to a concentrated aqueous solution\* of thiosemicarbazide. In the course of half an hour, a granular precipitate began to be deposited, and the solution was allowed to remain overnight. The granules, when collected and dried, were yellowish-white:

0.2864 gave 0.1171 Pt, 0.1719 AgCl, and 0.387 BaSO<sub>4</sub>.  
Pt=40.89; Cl=14.85; S=18.56.

0.0381 gave 6.2 c.c. N<sub>2</sub> at 30° and 760 mm. N=17.97.

C<sub>3</sub>H<sub>4</sub>N<sub>6</sub>Cl<sub>2</sub>S<sub>3</sub>Pt requires Pt=40.04; Cl=14.63; S=19.78;  
N=17.31 per cent.

#### *Summary and Conclusion.*

(1) Whilst mercuric chloride reacts with a mercaptan to yield a chloromercaptide, thus, R·SH + HgCl<sub>2</sub> = R·S·HgCl + HCl, cupric and platinic chlorides generally give mercaptides or mercaptides with only a slight admixture of chloromercaptides.

(2) Platinum in relation to monomercaptanic radicles functions either as tervalent or bivalent.

(3) The above chlorides bring about tautomeric changes in thio-carbamide and thioacetamide. Thiosemicarbazide with platinic chloride also undergoes similar transformation and yields a cyclic

degradation product,  $\begin{array}{c} \text{NH} \cdot \text{C} \cdot \text{SH} \\ \diagup \quad \diagdown \\ \text{N} \end{array}$ .

(4) The chloromercaptides of the potential mercaptans, inasmuch as they contain one or more imino-groups, are capable of fixing a molecule of hydrogen chloride, and in fact are hydrochlorides of complex bases.

CHEMICAL LABORATORY,  
COLLEGE OF SCIENCE,

UNIVERSITY OF CALCUTTA. [Received, June 21st, 1918.]

\* Thiosemicarbazide is almost insoluble in cold alcohol, ether, or acetone.

THE Council has ordered the following letter and report to be printed in the Journal of the Society:

WHINFIELD,  
SALCOMBE,  
S. DEVON.  
June 23rd, 1919.

GENTLEMEN,

I have the honour to submit a Report from the International Committee on Atomic Weights relative to such accounts of experimental work on atomic weights as have been published since their last regular Report of 1916, together with a table which it is suggested should be adopted in place of that now in use.

It will be seen that the Report deals with the atomic weights of hydrogen, carbon, bromine, boron, fluorine, lead, gallium, zirconium, tin, tellurium, yttrium, samarium, dysprosium, erbium, thorium, uranium, helium, and argon.

In the accompanying table for 1920, changes from the values hitherto adopted are recommended for argon, boron, gallium, thorium, and yttrium, and the atomic weight of nitrogen should be changed from 14.01 to the more precise value 14.008, which is probably accurate to within 1 in the third decimal place.

I am, Gentlemen,

Your obedient Servant,  
T. E. THORPE.

*The Hon. Secretaries,  
The Chemical Society,  
London.*

# Report of the International Committee on Atomic Weights for 1919-1920.

The last regular report of this committee, apart from an annual recommendation to continue the use of the table of atomic weights then presented, was published in 1916. The interruption in the series of reports was, of course, due to the world war, which created difficulties of a serious kind among all international organisations. Co-operation with Germany became impossible, partly because of the difficulties of correspondence and partly because of the personal hostilities created by the conduct of the war. There was also an inevitable slackening of scientific activities, and this was well shown by the unusually small number of new researches

in the field of atomic weights. Now that peace is in sight, it seems wise to resume the preparation of these reports, even though they may not be for some time yet quite so truly international as heretofore. The determinations published since the preparation of our last report may now be summarised, as follows:

*Hydrogen.*—A very thorough investigation by Burt and Edgar\* (*Phil. Trans.*, 1916, [A], 216, 393) on the volumetric composition of water has given the volume ratios of H to O as 2.00288:1. From this value, taking the normal litre weights of oxygen and hydrogen as 1.42900 and 0.089873 gram respectively, the atomic weight of hydrogen becomes 1.00772, or, rounded off, 1.0077. Guye (*J. Chim. Phys.*, 1917, 15, 208), from a discussion of Burt and Edgar's data, accepts this value, as lying between the two extremes of 1.00767 and 1.00773. If, however, instead of trusting to the densities of the gases and their physical constants exclusively we take into account the admirable researches of Morley, Noyes, and others upon the synthesis and analysis of water,† the most probable general mean for the atomic weight of hydrogen becomes 1.0078, which differs from the volumetric value by only 1/10,000. That is, the two distinct lines of attack upon the problem agree within the limits of actual uncertainty. For ordinary purposes, the approximate value 1.008 is close enough. It must be remembered that the tables prepared by this committee are for the use, not so much of specialists, as of working chemists in general, and too much refinement will only lead to confusion. No determinations of these or any other constants can be absolute and final. All are subject to errors which may be reduced nearly, but not quite, to insignificance, but never eliminated entirely. For example, in the determination of atomic weights from gaseous densities, it is not possible to guarantee the *absolute* purity of the gases or to avoid errors in weighing, in reductions to a vacuum, or in the values given to the physical constants that are used in the final computations. Some of these errors may be so small as to be negligible, and in the aggregate they may tend either to reinforce or to compensate one another, but their extreme magnitude can be estimated with some approach to accuracy and expressed by means of the usual  $\pm$  sign. At present, an accuracy to within 1/10,000 is the best we can expect to obtain.‡

\* This research was noted in the previous report for 1917. Its review by Guye renders its repetition desirable here.

† Computation by F. W. C.

‡ For an elaborate discussion of sources of error in atomic weight determinations, see Guye and his colleagues (MM. Germann, Moles, and Renard) in *J. Chim. Phys.*, 1916, 14, 25, 195, 204; 1917, 15, 60, 360, 405; 1918, 16, 46.

*Carbon*.—Two investigations on the atomic weight of carbon were reported from the Geneva laboratory in 1918. First, Stahr-foss (*J. Chim. Phys.*, 1918, **16**, 175) determined the density of acetylene, ethane, and ethylene. Acetylene proved to be unsatisfactory, because of its tendency to polymerise. From ethane he obtained the value  $C=12.006$ , and from ethylene  $C=12.004$ . On account of some uncertainties in the reductions, he prefers, provisionally, the value  $C=12.00$ .

Secondly, Batuecas (*J. Chim. Phys.*, 1918, **16**, 322) determined the density of ethane, and reduced his observations by three methods, giving  $C=12.005$ , 11.999, and 11.996. The last two, being concordant, he regards as preferable, and their mean,  $C=11.998$ , he adopts. It will be remembered that Richards and Hoover, by purely chemical methods, found  $C=12.005$ , and a later combination of all determinations published before 1918 gave the chairman of the committee the mean value  $C=12.0025$ . For ordinary purposes, the rounded-off value  $C=12.00$  may be used, and is so given in the table.

*Bromine*.—Three sets of determinations of the molecular weight of hydrobromic acid have been made in Guye's laboratory at Geneva by Moles (*J. Chim. Phys.*, 1916, **14**, 389. See review by Guye in the same number, p. 361), Reiman (*J. Chim. Phys.*, 1917, **15**, 293), and Murray (*J. Chim. Phys.*, 1917, **15**, 334. Reiman and Murray assume  $H=1.008$ ; Moles prefers 1.0076). The acid used was prepared by several distinct methods, and all gave concordant results, which may be summarised as follows, when  $H=1.0078$ :

	Mol. wt. HBr.	At. wt. Br.
Moles.....	80.9332	79.9254
Reiman.....	80.932	79.9242
Murray .....	80.930	79.9222

These values are wonderfully concordant, and the variations are far within the allowable limits of experimental error. In a recent combination, by the chairman of this committee, of all the available data relative to the atomic weight of bromine, the value found was  $Br=79.9228$ , in complete harmony with the Geneva determinations. For ordinary purposes, the rounded-off figure 79.92 is enough.

*Boron and Fluorine*.—In a very original investigation, Smith and Van Haagen (*Carnegie Inst. Washington, Publ.* No 267, 1918) have simultaneously redetermined the atomic weights of boron and fluorine. Their starting point was anhydrous borax,  $Na_2B_4O_7$ , and their chief difficulty was in insuring the complete dehydration of that compound. The salt was then converted, in a series of

successive experiments, into sodium sulphate, carbonate, nitrate, chloride, and fluoride, which gave eight independent values for boron ranging from  $B=10.896$  to  $10.905$ ; in mean,  $10.900$ . This value was computed with  $Na=22.997$ ,  $Cl=35.457$ ,  $S=32.064$ ,  $N=14.010$ , and  $C=12.005$ . The authors finally discuss all previous determinations, and show wherein they were affected by errors. The new value,  $10.900$ , should be adopted as the most probable.

In this research, sodium fluoride was compared, not only with borax, but also with the sulphate, and the eight values found ranged from  $F=19.002$  to  $19.008$ ; in mean,  $19.005$ . The rounded-off value,  $F=19$ , may be retained for all practical purposes.

*Lead.*—Echsner de Coninck and Gérard (*Compt. rend.*, 1916, 163, 514) have attempted to determine the atomic weight of lead by calcination of the nitrate, and find  $Pb=206.98$ , when  $N_2O_5=108$ . This determination is evidently of no present value. With this exception, the other recent researches relative to this constant have referred to isotopic lead, and the normal element is considered only in comparison with it. Richards and Wadsworth (*J. Amer. Chem. Soc.*, 1916, 38, 2613), for instance, find for normal lead  $Pb=207.183$ , and Richards and Hall (*J. Amer. Chem. Soc.*, 1917, 39, 537) give  $Pb=207.187$ , values slightly lower than the accepted  $207.20$  as determined by Baxter and Grover. Similar determinations by A. L. Davis (*J. Physical Chem.*, 1918, 22, 631) gave discordant results. As for isotopic lead, its atomic weight, is so variable as to show that it is nearly, if not always, a mixture of isotopes, and not a constant which can as yet be placed in the table. The values found have very great significance, but they are far from final.\*

*Gallium.*—By the analysis of carefully purified gallium chloride, Richards, Craig, and Sameshima (*Proc. Nat. Acad. Sci.*, 1918, 4, 387) find  $Ga=70.09$  and  $70.11$ . These determinations, however, are only preliminary, but they justify the provisional adoption of the value  $70.10$ . The original values given by the determinations of Lecoq de Boisbaudran vary from  $69.70$  to  $70.12$ , the last one being very near the new value.

*Zirconium.*—From the ratios between zirconium chloride and silver, Venable and Bell (*J. Amer. Chem. Soc.*, 1917, 39, 1598) find  $Zr=91.76$ . Although this determination is regarded as preliminary, the authors, by pointing out sources of error in all previous values, believe the new one to be the most probable. It

\* For discussions regarding the atomic weight of isotopic lead, see the Presidential address of Richards before the American Association for the Advancement of Science in December, 1918. Also F. W. Clarke, *Proc. Nat. Acad. Sci.*, 1918, 4, 181.

seems best, however, to await the complete investigation before changing the value heretofore accepted.

*Tin*.—Baxter and Starkweather (*Proc. Nat. Acad. Sci.*, 1916, **2**, 718), by electrolyses of stannic chloride, find  $\text{Sn}=118.703$  when  $\text{Cl}=35.457$ . This is in complete agreement with Briscoe's determination,  $\text{Sn}=118.698$ . The value 118.70 has already been adopted by the committee.

*Tellurium*.—Staehler and Tesch (*Zeitsch. anorg. Chem.*, 1916, **98**, 1), from careful syntheses of tellurium dioxide, find  $\text{Te}=127.51$ , which is confirmatory of the accepted value, 127.5.

*Yttrium*.—Hopkins and Balke (*J. Amer. Chem. Soc.*, 1916, **38**, 2332), by conversion of  $\text{Yt}_2\text{O}_3$  into  $\text{Yt}_2\text{Cl}_3$ , find  $\text{Yt}=88.9$ . The ordinary sulphate method is shown to be inaccurate. In a later investigation, Kremers and Hopkins (*J. Amer. Chem. Soc.*, 1919, **41**, 718) determined the ratio between yttrium chloride and silver, and found  $\text{Yt}=89.33$ . Since this method is the most trustworthy, the value given by it should be adopted. The other sulphate determinations are questionable.

*Samarium*.—The atomic weight of samarium has been determined by Stewart and James (*J. Amer. Chem. Soc.*, 1917, **39**, 2605) from the ratio between the chloride and silver. The value found is 150.44, which is essentially that given in the table. No change is needed.

*Dysprosium*.—Engle and Balke (*J. Amer. Chem. Soc.*, 1917, **39**, 67), by conversion of the oxide into the chloride, found  $\text{Dy}=164.228$ . Later, by the same method, Kremers, Hopkins, and Engle (*J. Amer. Chem. Soc.*, 1918, **40**, 598) found  $\text{Dy}=163.83$ . This discordance, like that already shown for yttrium, led the last-named chemists to determine the ratio between dysprosium chloride and silver, which gave 162.52. The earlier method is discredited, and the last value, rounded to 162.5, seems to be the one best entitled to acceptance.

*Erbium*.—For this element, by the oxide-chloride method, Wichers, Hopkins, and Balke (*J. Amer. Chem. Soc.*, 1918, **40**, 1615) obtained values ranging from  $\text{Er}=168.00$  to 168.84. The method of determination is thus again shown to be untrustworthy.

*Thorium*.—In a long series of concordant analyses of thorium bromide, Hönigschmid (*Zeitsch. Elektrochem.*, 1916, **22**, 18) finds  $\text{Th}=232.152$  from the silver ratio and 232.150 from the silver chloride ratio when  $\text{Br}=79.916$ . The value  $\text{Th}=232.15$  should be adopted for general use. He also studied thoria from uranium ores which contained ionium. For this mixture, he obtained an atomic weight slightly in excess of 231.50. This may be approximate to the unknown atomic weight of ionium.

*Uranium.*—The latest series of determinations of the atomic weight of uranium by Hönigschmid and Horovitz (*Monatsh.*, 1916, 37, 185) was based, like their earlier series, upon analyses of the tetrabromide. Two sets of analyses were made, one upon a bromide which had been fused in bromine vapour, the other in nitrogen. The value obtained ranged from  $U=238.04$  to  $238.16$ , the latter being in harmony with their former determinations. The rounded figure,  $238.2$ , is given in the table.

*Helium.*—Taylor (*Physical Rev.*, 1917, 10, 653), using the microbalance in determining the density of helium, finds  $He=4.0008$ . Guye (*J. Chim. Phys.*, 1918, 16, 46), in a recalculation of the data, finds  $He=3.998$ . The value 4 should be retained.

*Argon.*—From the density and compressibility of argon, Leduc (*Compt. rend.*, 1918, 167, 70) finds  $A=39.91$ . He regards the second decimal as uncertain, and advises the adoption of the rounded value  $39.9$ .

In the following table of atomic weights proposed for 1920, few changes have been made from the values given in the last preceding table. The new values are:  $A=39.9$ ,  $B=10.9$ ,  $Ga=70.1$ ,  $Th=232.15$ , and  $Yt=89.33$ . In addition to these, the atomic weight of nitrogen should be changed from  $14.01$  to the more precise value  $N=14.008$ . The latter figure represents all the best determinations, and is probably correct to within 1 in the third decimal place. For so small a value, the change is insignificant.

(Signed) F. W. CLARKE.  
T. E. THORPE.  
G. URBAIN.

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1920.

*International Atomic Weights.*

	Symbol.	Atomic weight.		Symbol.	Atomic weight.
Aluminium .....	Al	27.1	Molybdenum .....	Mo	96.0
Antimony .....	Sb	120.2	Neodymium .....	Nd	144.3
Argon .....	A	39.9	Neon .....	Ne	20.2
Arsenic .....	As	74.96	Nickel .....	Ni	58.68
Barium .....	Ba	137.37	Niton (radium emanation) .....	Nt	222.4
Bismuth .....	Bi	208.0	Nitrogen .....	N	14.008
Boron .....	B	10.9	Osmium .....	Os	190.9
Bromine .....	Br	79.92	Oxygen .....	O	16.00
Cadmium .....	Cd	112.40	Palladium .....	Pd	106.7
Cæsium .....	Cs	132.81	Phosphorus .....	P	31.04
Calcium .....	Ca	40.07	Platinum .....	Pt	195.2
Carbon .....	C	12.00	Potassium .....	K	39.10
Cerium .....	Ce	140.25	Praseodymium .....	Pr	140.9
Chlorine .....	Cl	35.46	Radium .....	Ra	226.0
Chromium .....	Cr	52.0	Rhodium .....	Rh	102.9
Cobalt .....	Co	58.97	Rubidium .....	Rb	85.45
Columbium .....	Cb	93.1	Ruthenium .....	Ru	101.7
Copper .....	Cu	63.57	Samarium .....	Sa	150.4
Dysprosium .....	Dy	162.5	Scandium .....	Sc	44.1
Erbium .....	Er	167.7	Selenium .....	Se	79.2
Europium .....	Eu	152.0	Silicon .....	Si	28.3
Fluorine .....	F	19.0	Silver .....	Ag	107.88
Gadolinium .....	Gd	157.3	Sodium .....	Na	23.00
Gallium .....	Ga	70.1	Strontium .....	Sr	87.63
Germanium .....	Ge	72.5	Sulphur .....	S	32.06
Glucinum .....	Gl	9.1	Tantalum .....	Ta	181.5
Gold .....	Au	197.2	Tellurium .....	Te	127.5
Helium .....	He	4.00	Terbium .....	Tb	159.2
Holmium .....	Ho	163.5	Thallium .....	Tl	204.0
Hydrogen .....	H	1.008	Thorium .....	Th	232.15
Indium .....	In	114.8	Thulium .....	Tm	168.5
Iodine .....	I	126.92	Tin .....	Sn	118.7
Iridium .....	Ir	193.1	Titanium .....	Ti	48.1
Iron .....	Fe	55.84	Tungsten .....	W	184.0
Krypton .....	Kr	82.92	Uranium .....	U	238.2
Lanthanum .....	La	139.0	Vanadium .....	V	51.0
Lead .....	Pb	207.20	Xenon .....	Xe	130.2
Lithium .....	Li	6.94	Ytterbium (Neoytterbium) .....	Yb	173.5
Lutecium .....	Lu	175.0	Yttrium .....	Yt	89.33
Magnesium .....	Mg	24.32	Zinc .....	Zn	65.37
Manganese .....	Mn	54.93	Zirconium .....	Zr	90.6
Mercury .....	Hg	200.6			



LXXIII.—*The Presence of Aconitic Acid in Sugar-cane Juice and a New Reaction for the Detection of the Acid.*

By CHARLES SOMERS TAYLOR.

AMONG the non-saccharine substances existing in sugar-juice, Geerligs mentions certain acids which are undoubtedly present. He states, however, that the question of the presence of aconitic acid requires further investigation ("Cane Sugar and the Process of its Manufacture," 1909, p. 51). This acid is generally supposed to have been detected first in the juice of the sugar-cane by Behr (*Ber.*, 1877, 10, 351). There is no doubt that Behr discovered large quantities of aconitic acid in muscovado sugar and molasses, from both of which he obtained the acid, the composition of which he verified by combustion and also by the formation of a silver salt of known composition. He also appears to have examined the action of lime on invert-sugar in order to find whether the acid can have been formed in the process of manufacture, and states that none of the acid was produced in any of his experiments. As the latter evidence was merely negative, however, he obtained from Cuba some sugar-juice sterilised with phenol, which he examined in Germany. His deduction that aconitic acid was present in this sugar-cane juice was based on the fact that he obtained the lead and acid ammonium salts in their characteristic form. The real criteria of analysis and melting-point determinations were omitted, and he lost the cleanest portion of his acid by accident, whilst some of the partly clean substance obtained by him melted at  $167^{\circ}$ , or more than  $20^{\circ}$  below the true melting point of aconitic acid. His evidence, therefore, of the actual existence of this acid in quantity in the juice in its natural state appeared to require further corroboration before it could be said to be conclusive.

The most interesting point to the sugar manufacturer as regards the existence of this acid is that it forms a calcium salt which dissolves readily in cold water, but is almost entirely insoluble in hot. It is therefore liable to be precipitated on the tubes of the evaporating plant unless care is taken to keep the juice hot while filtering.

EXPERIMENTAL.

As it was thought possible that the acid might be a product of disease in the cane, two samples of juice were employed, one from

diseased and one from ordinary cane. Both samples were precipitated with basic lead acetate. The precipitate was then washed, suspended in water, and decomposed in the usual manner with hydrogen sulphide. After filtration, the water was evaporated in a vacuum, and the crystalline residue extracted with ether. The portion insoluble in ether was mostly malic acid. The crude aconitic acid from the ethereal solution was purified by reprecipitating with lead acetate and decomposing the precipitate with hydrogen sulphide. Small quantities of aconitic acid were obtained from the juice of the ordinary canes, but the diseased canes gave a viscid substance by this treatment, from which it was found impossible to crystallise the acid.

*Examination of the Acid.*—The mean of two determinations of the equivalent weight of the acid gave the value 58.55. The quantities taken were very small, so that the method was subject to large error.

The acid melted and decomposed at  $191^{\circ}$  (corr.), which is the melting point of aconitic acid. (Found: C=41.38; H=3.95\*; C=41.01; H=3.65.  $C_6H_6O_6$  requires C=41.38; H=3.45 per cent.)

*Qualitative Experiments: A New Colour Test for Aconitic Acid and, indirectly, for Citric Acid.*

The usual qualitative tests were carried out with the acid in order to identify it as aconitic acid, although these tests had already been performed by Behr. The calcium salt was obtained as a heavy, white precipitate on boiling a solution of the sodium salt with calcium chloride. It was interesting to note that unless the boiling was protracted, this precipitate dissolved immediately on cooling. After protracted boiling, however, the gelatinous precipitate appeared to change into a crystalline form, which was insoluble even after cooling.

A very delicate test for aconitic acid was discovered in examining the action of acetic anhydride on it. On the addition of this reagent to a small quantity of the acid, a pink coloration appeared, which rapidly turned to deep red and then to magenta. Further heating produced a bluish-green liquid, finally turning to a brown, almost opaque, solution. The red liquid first obtained, if the action is checked by cooling, shows a spectrum entirely in the red, absorbing all other rays almost completely. In the intermediate

\* This abnormally high result for hydrogen was probably due to the fact that the combustion was made in India in the middle of the rains, on a day when the air was nearly saturated.

stage, when the magenta liquid was obtained, it appeared to consist of a solution of two coloured substances, namely, a red one which was soluble in water and a blue one which dissolved readily in ether. The two could be easily separated by shaking the acetic anhydride solution with water and ether, when the aqueous layer became red and the ethereal solution blue.

Many attempts were made to isolate these red and blue compounds, but they appear to be exceedingly unstable, being rapidly destroyed by water, acids, or alkalis.

The substance obtained in this way is intensely highly coloured. The intensity of the colour is so great, in fact, that the faintest trace of aconitic acid will produce a strong colour. The minimum quantity necessary to obtain the colour was determined as follows.

One gram of aconitic acid was dissolved in a litre of water, and various fractions of a milligram were obtained by appropriate dilutions and evaporation to dryness in porcelain basins. To the residue a few drops of acetic anhydride were added, and the whole was heated on a water-bath. The results are tabulated below:

Aconitic acid. Milligram.	Colour obtained.
1.0	Intense, appearing almost immediately.
0.1	Strong tinge rather slower in appearance.
0.02	Faint colour taking some time to appear.
0.01	Faint colour just perceptible after some time.

That this reaction was due to aconitic acid alone, and not to the other acids present in sugar-cane juice, was proved positively by examining pure aconitic acid from another source, which gave the same results as that obtained from sugar-cane juice. It was also proved negatively by showing that none of the other acids present in sugar-cane gives the reaction. Citric acid, however, may be detected by the action of acetic anhydride after gentle fusing in a test-tube. By this means, traces of aconitic acid are obtained which at once give the colour reaction. Citric acid itself does not give the reaction.

By this colour test, it was also proved that aconitic acid exists as a salt in sugar-cane juice, and not in the free state. This was done by shaking with ether sugar-cane juice, in the ordinary state and after treatment with dilute sulphuric acid. The ethereal extract in both cases was evaporated to dryness, and the residue heated on a water-bath with acetic anhydride. The extract from the untreated juice gave no reaction whatever, whilst that from the juice which had been treated with sulphuric acid gave the intense red characteristic of aconitic acid.

*The Nature of the Colour Reaction between Acetic Anhydride and Aconitic Acid.*

That the colour reaction takes place by condensation of the carboxyl groups of the acid is almost certainly proved by the fact that ethyl aconitate, when treated with acetic anhydride, gives no colour whatever.

Treatment of itaconic, citraconic, and mesaconic acids also gave no colour. It was therefore inferred that very little decomposition of the molecule takes place during the reaction, but that the change was probably one of rearrangement of the carbon atoms with, possibly, some removal of water, addition of acetic anhydride, or both actions together.

As has been already mentioned, the actual coloured substance is extremely unstable. Evaporation of the acetic anhydride solution in a vacuum over sodium hydroxide, and subsequent washing with ether, gives a brown substance, which appears to be micro-crystalline. No definite crystals were obtained. Analysis of this brown substance gave the following figures:

Found: C=51.63; H=2.93.

$C_6H_4O_4$  requires C=51.43; H=2.86 per cent.

The substance does not appear to resemble any of the known compounds of this formula. Its deep yellowish-brown colour resembles that of 2:5-dihydroxybenzoquinone, but it appears to be more unstable than that substance. All that can be said for the present, therefore, is that the brown substance has many properties which would point to its having a quinonoid structure, but that this is not proved.

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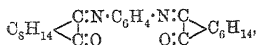
[Received, January 6th, 1919.]

LXXIV.—*Studies in the Camphane Series. Part XXXVII. Aryl Derivatives of Imino- and Amino-camphor.*

By MARTIN ONSLOW FORSTER and HANS SPINNER.

THE highest recorded molecular rotation is that of *p*-phenylenebis-iminocamphor, which has  $[M]_D$  6173° in a pyridine solution containing 0.624 gram in 100 c.c. (Forster and Thornley, T., 1909, 95, 942). In this compound there appears to be presented, within a relatively

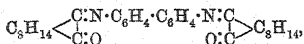
narrow molecular compass, the optimum association of azethenoid groups, conjugated linkings, and a benzene ring,



required for exaltation of the optical activity due originally to the camphor nucleus.

With a view to extending this field of inquiry we prepared a selection of similar compounds, but since none of these, with one exception, approached the foregoing substance in optical activity, they have been described only in a dissertation (Hans Spinner, Zürich, 1912). Several of them having now been prepared by Singh and Mazumder (this vol., 566), who did not have access to the publication in question, we desire to record the properties of the remainder.

The only derivative of this class having optical activity nearly so high as that displayed by *p*-phenylenebisiminocamphor is *pp*-di-phenylenebisiminocamphor,



prepared from benzidine and camphorquinone. It occurs in two forms, (1) yellowish-green, melting at 276° and having  $[\text{M}]_D$  5565°, and (2) golden-brown, melting at 274° with  $[\text{M}]_D$  5360°. In this compound the same exaltation factors are noticeable, but they operate in a slightly less confined molecular environment, which may account for the somewhat diminished optical activity.

It has not been possible permanently to convert either of these compounds into the corresponding derivative of aminocamphor, but the substituted iminocamphors of more simple structure are easily so converted; there is then observed the same profound depression in optical activity already noticed in similar examples (F. and T., *loc. cit.*), as indicated by the following measurements in chloroform at 20°:

	$[\alpha]_D$	$[\text{M}]_D$	Difference of $[\text{M}]_D$
$\alpha$ -Naphthyliminocamphor .....	628°	1828°	—
$\alpha$ -Naphthylaminocamphor .....	115	338	1490°
$\beta$ -Naphthyliminocamphor .....	720	2096	—
$\beta$ -Naphthylaminocamphor .....	140	411	1685
<i>o</i> -Chlorophenyliminocamphor ...	153	423	—
<i>o</i> -Chlorophenylaminocamphor ...	94	262	161
<i>m</i> -Chlorophenyliminocamphor ...	499	1374	—
<i>m</i> -Chlorophenylaminocamphor ...	118	328	1046
<i>m</i> -Carboxyphenyliminocamphor .	470	1341	—
<i>m</i> -Carboxyphenylaminocamphor .	127	364	975
<i>p</i> -Carboxyphenyliminocamphor...	423	1205	—
<i>p</i> -Carboxyphenylaminocamphor	121	347	858

The one exception is *o*-chlorophenyliminocamphor, because it has by far the lowest optical activity yet recorded in this series, namely,  $[M]_D 423^\circ$ , whilst none of the other members, even the *m*- or *p*-chloro-derivative, has  $[M]_D$  less than  $1000^\circ$ ; it is probable that this abnormality is due to partial saturation of the azethenoid or carbonyl group by supplemental valency of the chlorine atom in an ortho-position.

Although arylamines generally undergo condensation with camphorquinone very readily, some exceptions, in addition to that of *p*-nitroaniline, have been observed; these are *o*-aminobenzoic acid, *o*-aminophenol, 2:4-diaminophenol, 2:4:6-triaminophenol, picramide, picramic acid, 4-nitro- $\alpha$ -naphthylamine, and 5-nitro- $\alpha$ -naphthylamine, from none of which has the corresponding derivative of iminocamphor been obtained.

#### EXPERIMENTAL.

$\alpha$ - and  $\beta$ -Naphthylaminocamphor,  $C_8H_{14} \begin{matrix} \text{CH} \cdot \text{NH} \cdot C_{10}H_7 \\ | \\ \text{CO} \end{matrix}$ .

$\alpha$ -Naphthyliminocamphor, with  $[\alpha]_D 628.2^\circ$  in chloroform, also prepared by Singh and Mazumder (this vol., 573), was shaken in ethereal solution with 10 per cent. potassium hydroxide and zinc dust until the colour had disappeared, when the ether deposited a white residue of  $\alpha$ -naphthylaminocamphor on evaporation. Recrystallisation from hot alcohol gave transparent, four-sided prisms melting at  $165^\circ$ :

0.1760 gave 0.5276  $CO_2$  and 0.1251  $H_2O$ .  $C=81.76$ ;  $H=7.90$ .

$C_{20}H_{23}ON$  requires  $C=81.91$ ;  $H=7.85$  per cent.

The product is readily soluble in benzene, chloroform, ethyl acetate, or boiling acetone, moderately so in cold acetone or alcohol; it is insoluble in cold light petroleum, which dissolves it sparingly when boiled. A solution containing 0.1215 gram in 25 c.c. of chloroform gave  $\alpha_D 1^\circ 41'$  in the 3-dcm. tube, whence  $[\alpha]_D 115.5^\circ$ .

$\beta$ -Naphthyliminocamphor, with  $[\alpha]_D 720.5^\circ$  (compare S. and M., this vol., 573), was treated in the same way, and the resulting  $\beta$ -naphthylaminocamphor crystallised from alcohol in colourless, flattened, four-sided plates melting at  $157$ – $158^\circ$ :

0.2305 gave 0.6896  $CO_2$  and 0.1631  $H_2O$ .  $C=81.59$ ;  $H=7.86$ .

The base is insoluble in cold light petroleum, but dissolves readily in other organic media. A solution containing 0.1255 gram in 25 c.c. of chloroform gave  $\alpha_D 2^\circ 7'$  in the 3-dcm. tube, whence  $[\alpha]_D 140.5^\circ$ .

*o*- and *m*-Chlorophenyliminocamphor,  $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{NH} \cdot C_6H_4\text{Cl} \\ | \\ \text{CO} \end{smallmatrix}$ .

*o*-Chlorophenyliminocamphor, with  $[\alpha]_D 153.4^\circ$  (compare S. and M., this vol., 572), gave *o*-chlorophenylaminocamphor melting at  $148^\circ$  after crystallisation from hot alcohol, which deposits it in colourless, transparent prisms:

0.2174 gave 0.5508  $CO_2$  and 0.1431  $H_2O$ .  $C=69.10$ ;  $H=7.31$ .

0.1982 „ 0.1013 AgCl.  $Cl=12.64$ .

$C_{16}H_{20}ONCl$  requires  $C=69.16$ ;  $H=7.26$ ;  $Cl=12.77$  per cent.

It is readily soluble in organic media other than alcohol and petroleum, which dissolve it less freely. A solution containing 0.1236 gram in 25 c.c. of chloroform gave  $\alpha_D 1^\circ 24'$  in the 3-dcm. tube, whence  $[\alpha]_D 94.4^\circ$ .

*m*-Chlorophenyliminocamphor, with  $[\alpha]_D 498.8^\circ$  (S. and M., *loc. cit.*), gave *m*-chlorophenylaminocamphor melting at  $98-99^\circ$  after crystallisation from diluted alcohol, whence it separates in colourless aggregates of indefinite structure:

0.1726 gave 0.4368  $CO_2$  and 0.1129  $H_2O$ .  $C=69.02$ ;  $H=7.27$ .

0.2158 „ 0.1106 AgCl.  $Cl=12.68$ .

It is more readily soluble than the isomeride. A solution containing 0.1234 gram in 25 c.c. of chloroform gave  $\alpha_D 1^\circ 45'$  in the 3-dcm. tube, whence  $[\alpha]_D 118.2^\circ$ .

*m*- and *p*-Carboxyphenyliminocamphor,  $C_8H_{14} \begin{smallmatrix} \text{C} \cdot \text{N} \cdot C_6H_4 \cdot \text{CO}_2\text{H} \\ | \\ \text{CO} \end{smallmatrix}$ .

Camphorquinone and *m*-aminobenzoic acid in molecular proportion were heated in alcohol during three hours, when the product, after recrystallisation from diluted alcohol, formed pale yellow leaflets melting at  $195.5^\circ$ :

0.3273 gave 15.4 c.c.  $N_2$  at  $29^\circ$  and 763 mm.  $N=5.21$ .

$C_{17}H_{19}O_3N$  requires  $N=4.91$  per cent.

It is readily soluble in alcohol, acetone, chloroform, ethyl acetate, or boiling benzene, but is insoluble in light petroleum. A solution containing 0.1218 gram in 25 c.c. gave  $\alpha_D 4^\circ 35'$  in the 2-dcm. tube, whence  $[\alpha]_D 470.4^\circ$ .

The isomeride prepared from camphorquinone and *p*-aminobenzoic acid separated from diluted alcohol in small, brownish-yellow prisms melting at  $237^\circ$  and resembling the *m*-compound in solubility:

0.4210 gave 19.0 c.c.  $N_2$  at  $21^\circ$  and 758 mm.  $N=5.15$ .

A solution containing 0.1217 gram in 25 c.c. of chloroform gave  $\alpha_D 4^\circ 7'$  in the 2-dcm. tube, whence  $[\alpha]_D 422.8^\circ$ .

*m*- and *p*-Carboxyphenylaminocamphor,  $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{NH} \cdot C_6H_4 \cdot CO_2H \\ \text{CO} \end{smallmatrix}$ .

The foregoing substances dissolve in aqueous alkali hydroxide, and when the solutions are shaken with zinc dust, filtered, and acidified, the corresponding derivative of aminocamphor is liberated. The *m*-compound separates from diluted alcohol in colourless needles melting at 210—211°:

0.1630 gave 0.4237  $CO_2$  and 0.1075  $H_2O$ .  $C = 70.89$ ;  $H = 7.33$ .

$C_{17}H_{21}O_3N$  requires  $C = 71.08$ ;  $H = 7.32$  per cent.

It dissolves readily in acetone, chloroform, or ethyl acetate, less readily in alcohol, being only moderately soluble in benzene and insoluble in petroleum. A solution containing 0.1235 gram in 25 c.c. of chloroform gave  $\alpha_D 1^\circ 53'$  in the 3-dcm. tube, whence  $[\alpha]_D 127.1^\circ$ .

The *p*-compound crystallises from diluted alcohol in colourless aggregates melting at 239° after slight shrinking and discoloration:

0.1951 gave 0.5081  $CO_2$  and 0.1287  $H_2O$ .  $C = 71.03$ ;  $H = 7.33$ .

In solubility it resembles the isomeride. A solution containing 0.1207 gram in 25 c.c. of chloroform gave  $\alpha_D 1^\circ 45'$  in the 3-dcm. tube, whence  $[\alpha]_D 120.8^\circ$ .

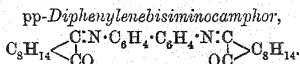
*p*-Acetylaminophenyliminocamphor,  $C_8H_{14} \begin{smallmatrix} C:N \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3 \\ CO \end{smallmatrix}$ .

Camphorquinone and *p*-aminoacetanilide in molecular proportion dissolved in alcohol were heated under reflux during four hours, the product crystallising on dilution in yellow, six-sided plates melting at 211—212°:

0.2166 gave 17.8 c.c.  $N_2$  at 21° and 771 mm.  $N = 9.53$ .

$C_{18}H_{22}O_2N_2$  requires  $N = 9.40$  per cent.

It is readily soluble in alcohol, acetone, chloroform, or ethyl acetate, dissolving with difficulty in cold benzene or hot petroleum; it is insoluble in the last-named when cold. A solution containing 0.1220 gram in 25 c.c. of chloroform gave  $\alpha_D 8^\circ 25'$  in the 2-dcm. tube, whence  $[\alpha]_D 862.4^\circ$  and  $[M]_D 2570^\circ$ .



Camphorquinone (6.6 grams) and benzidine (3.6 grams) dissolved in alcohol (80 c.c.) were heated under reflux during six hours, when the liquid deposited two distinguishable forms of crystals on cooling;



these were separated mechanically and also by fractional crystallisation, when the less soluble component, formed in preponderating amount, consisted of longitudinal clusters of minute, yellowish-green prisms melting at 276°:

0.2599 gave 0.7606 CO<sub>2</sub> and 0.1785 H<sub>2</sub>O. C=79.81; H=7.63.

0.2680 „ 13.4 c.c. N<sub>2</sub> at 22° and 765 mm. N=5.73.

C<sub>32</sub>H<sub>36</sub>O<sub>2</sub>N<sub>2</sub> requires C=80.00; H=7.50; N=5.83 per cent.

A solution containing 0.1231 gram in 25 c.c. of chloroform gave  $\alpha_D$  11°25' in the 2-dcm. tube, whence  $[\alpha]_D$  1159.3°.

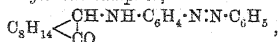
The more readily soluble modification crystallised in transparent, golden-brown needles melting at 274°:

0.1861 gave 0.5458 CO<sub>2</sub> and 0.1288 H<sub>2</sub>O. C=79.98; H=7.69.

A solution containing 0.1220 gram in 25 c.c. of chloroform gave  $\alpha_D$  10°54' in the 2-dcm. tube, whence  $[\alpha]_D$  1116.8°. Both forms yielded benzidine and camphorquinone on hydrolysis with alcoholic hydrochloric acid.

In addition to the foregoing substances we prepared *o*- and *p*-tolyliminocamphor and *p*-benzeneazophenyliminocamphor, which are described by Singh and Mazumder, and in the case of the last-named compound a discrepancy is noticeable. These authors obtained orange needles melting at 129—130° and giving  $[\alpha]_D$  550.4° in chloroform, whilst our product crystallised in silky, red needles melting at 135° and giving  $[\alpha]_D$  677.0°, whence  $[M]_D$  2335°.

*p*-Benzeneazophenylaminocamphor,

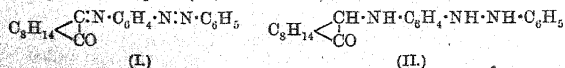


was obtained by shaking an ethereal solution of the iminocamphor derivative with zinc dust and 10 per cent. potassium hydroxide in a closed flask during several hours, when the colour was completely destroyed. On contact with air, however, the ethereal liquid immediately became orange, and on evaporation deposited a brownish-red mass which crystallised from alcohol in lustrous, dark brownish-red, three-cornered plates melting at 170°:

0.1272 gave 0.3538 CO<sub>2</sub> and 0.0826 H<sub>2</sub>O. C=75.86; H=7.21.

C<sub>22</sub>H<sub>25</sub>ON<sub>3</sub> requires C=76.08; H=7.20 per cent.

From these colour changes it would appear that benzeneazophenyliminocamphor (I) is first reduced to the colourless phenylhydrazinophenylaminocamphor (II; not isolated), which is then oxidised in air



to benzeneazophenylaminocamphor. Even very dilute solutions of the last-named substance were too dark for polarimetric measurement.

These experiments were carried out at the Royal College of Science, South Kensington, during the later months of 1911.

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[Received, July 3rd, 1919.]

## LXXV.—*The Oxidation of Coal.*

By FREDERICK VINCENT TIDESWELL and RICHARD VERNON  
WHEELER.

In a recent paper ("The Oxidation and Ignition of Coal," T., 1918, 113, 945) a hypothesis was advanced that the first step in the oxidation of coal is the formation of an additive compound, or complex, of oxygen with one or more of the substances present in coal.

Partington (*Chem. News*, 1919, 118, 50) has suggested "that this hypothesis, which is of itself not very probable, does not account for the observed results, and that it should be replaced by another hypothesis," based primarily on known physical phenomena, which appears to be somewhat as follows.

(1) The admission of air to newly-won coal, deprived of its occluded gases, results in the physical adsorption of both oxygen and nitrogen on the surface of the coal. The pressure of the air in contact with the coal will at first fall very rapidly for a short period, and will then gradually fall off until adsorption equilibrium is reached. If the adsorbed layer penetrates into the bulk of the adsorbent, this very slow final fall of pressure may go on for a long time.

(2) The adsorbed layer, being at high concentration, may subsequently react with the coal, possibly slowly, with the production of oxides of carbon.

(3) The formation of carbon monoxide and carbon dioxide in a constant ratio at a given temperature is explained on the assumption that carbon monoxide is formed first and subsequently reacts with water-vapour, the "water-gas equilibrium,"  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ , being attained.

This hypothesis in principle possesses the great merits of simplicity and of conformity with well-known phenomena. Had it been

possible to account so easily for the facts observed during the oxidation of coal, some such hypothesis would have been chosen in preference to that ultimately adopted.

The phenomena that occur during the oxidation of coal bear a striking resemblance to, and clearly have much in common with, the phenomena of the combustion of carbon.

Rhead and Wheeler (T., 1913, 103, 461) were faced with a similar difficulty to that which presents itself with coal when attempting to explain the results of their experiments on the combustion of carbon. They found that carbon at all temperatures up to  $900^{\circ}$ , and probably above that temperature, has the power of pertinaciously retaining oxygen. This oxygen cannot be removed by exhaustion alone, but only by increasing the temperature of the carbon during exhaustion. When quickly released in this manner, it appears, not as oxygen, but as carbon monoxide and carbon dioxide. Rhead and Wheeler concluded, after discussion of their experimental data at some length, that: "No physical explanation alone can account for this 'fixation' of oxygen, but, in all probability, it is the outcome of a physico-chemical attraction between oxygen and carbon. Physical, inasmuch as it seems hardly possible to assign any definite molecular formula to the complex formed, which, indeed, shows progressive variation in composition; chemical, in that no isolation of the complex can be effected by physical means."

In an account of earlier portions of the same research (T., 1912, 101, 846), the relationship between the carbon monoxide and carbon dioxide produced during the oxidation of carbon had been fully discussed. A comparison of the rates of reaction at different temperatures, between carbon and carbon dioxide, carbon and oxygen, and carbon monoxide and oxygen, with a study of the products of reaction, showed: (1) that some carbon monoxide is produced during the oxidation of carbon at low temperatures under conditions which do not admit of the reduction of carbon dioxide by carbon; on the other hand, (2) carbon dioxide is produced at low temperatures in quantity greater than can be accounted for on the supposition that carbon monoxide is first formed and then oxidised to carbon dioxide. The conclusion follows that when carbon is burnt at low temperatures, carbon monoxide and carbon dioxide are produced simultaneously.

The general conclusion reached by Rhead and Wheeler as regards the mode of combustion of carbon, to account for this simultaneous production of the two oxides, presumes the formation of a complex, as already stated, and partial decomposition of this complex as fresh oxygen molecules became attached, until the carbon becomes "saturated." The products of combustion during this period of satura-

tion are the complex, carbon dioxide, and carbon monoxide. After the carbon has become saturated there is an alternate formation and decomposition of the complex, and the only apparent products of combustion are carbon dioxide and carbon monoxide. These are produced in a fixed ratio dependent on the temperature of reaction. Drying of the oxygen by phosphoric oxide does not affect the formation of the complex, but retards its rate of decomposition (T., 1913, 103, 1310).

This explanation of the manner of burning of carbon is, we believe, accepted by the majority of chemists. A similar explanation of the manner of burning of coal at low temperatures could be advanced by analogy. To rely solely on such an analogy is, however, scarcely safe; for although there are, in all probability, compounds in coal resembling the carbon molecule in their structure (see Jones and Wheeler, T., 1916, 109, 709), there is no evidence of the presence of free carbon. Moreover, the fact that the compounds in coal are hydrogenated and that some may yield water on oxidation, introduces a complication from which research on the combustion of carbon is free.

Nevertheless, if the same methods of examining the action of oxygen on coal be followed as with carbon, a similar conclusion will be reached: an hypothesis of physical adsorption of the oxygen, followed by direct formation of carbon monoxide, and, subsequently, of carbon dioxide is inadequate to explain quantitatively the results obtained; although it may, at first sight, afford a plausible explanation of the phenomena qualitatively.

A comparison of the amount of adsorption of inert gases, such as nitrogen, by coal with the amount of oxygen absorbed thereby shows the two actions to be not only of a different order but to be affected by temperature in a different sense.

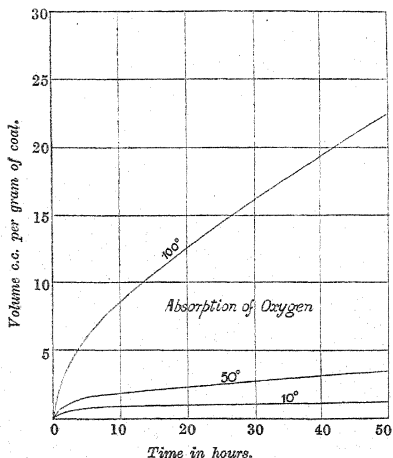
The adsorption of gases by coal has been studied by several chemists; for example, Graham (*Trans. Inst. Min. Eng.*, 1917, 52, 388) and Katz (*U.S. Bureau of Mines, Tech. Paper 147*; Washington, 1917). Graham obtained the following figures for the quantities of different gases adsorbed or, as he terms it, "dissolved," by the same sample of coal-dust (of 200-mesh fineness):

Temperature.	Volume of gas adsorbed per gram of coal. C.c measured at N.T.P.				
	H <sub>2</sub> .	N <sub>2</sub> .	CO.	CH <sub>4</sub> .	CO <sub>2</sub> .
30° .....	0.068	0.576	0.712	—	8.00
100° .....	0.038	0.115	0.159	0.476	1.48

As regards oxygen, Graham's own words may be quoted: "The solubility of oxygen—as distinct from the ordinary (chemical) absorption by coal—has also been determined for a sample of

oxidised coal-dust, it being, of course, impossible to determine the solubility in unoxidised coal directly. The sample used had been oxidised for about fourteen days at  $100^{\circ}$ , and even after this a slight absorption at  $30^{\circ}$  still took place. For this, however, a correction could be made, and with this it was found that oxygen was soluble in the oxidised sample of coal-dust (of 200-mesh fineness) to the extent of about 40 c.c. per 100 gram when the percentage of oxygen over the dust equalled 100. The solubility of nitrogen in the same sample was found to be equal to approximately 35 c.c. for

FIG. 1.



100 per cent. nitrogen per 100 gram of coal. The figure for the solubility of nitrogen in unoxidised coal for similar concentration was 57.6. It is highly probable, therefore, that the solubility of oxygen in unoxidised coal will be somewhere about 65 c.c. in pure oxygen per 100 gram of coal."

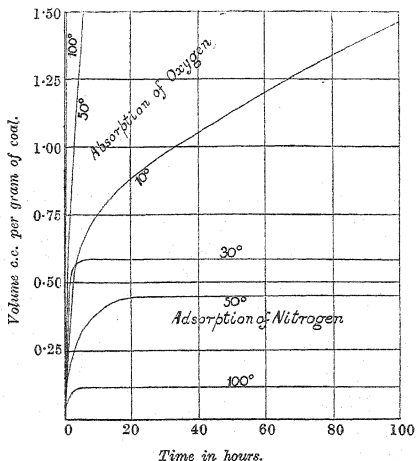
These results for different gases are in agreement with the determinations made of the adsorption of gases by charcoal by Homfray (*Zeitsch. physikal. Chem.*, 1910, **74**, 129), who showed that the amounts adsorbed are proportional to the boiling points of the gases.

In Fig. 1 are given time-volume curves for the absorption of

oxygen by fresh coal (of 10-mesh fineness and deprived of its occluded gases) at  $10^{\circ}$ ,  $50^{\circ}$ , and  $100^{\circ}$ ; and in Fig. 2 the same curves are reproduced on a different scale for comparison with adsorption curves for nitrogen at  $30^{\circ}$ ,  $50^{\circ}$ , and  $100^{\circ}$ . The nitrogen curve at  $50^{\circ}$  was obtained with a sample of the same coal as was used for the absorption of oxygen; the curves at  $30^{\circ}$  and  $100^{\circ}$  are constructed from Graham's data (obtained with a coal of 200-mesh fineness).

Increase of temperature is thus shown to cause a rapid increase in

FIG. 2.



the rate of absorption of oxygen by coal, and an increase in the total amount absorbed (compare also Winmill, *Trans. Inst. Min. Eng.*, 1913, **46**, 3, 559; 1914, **48**, 514). On the other hand, the quantity of a gas physically adsorbed decreases as the temperature is increased.

Even at the ordinary atmospheric temperature the amount of absorption of oxygen by coal is greater than can be accounted for by adsorption phenomena; and the higher the temperature the greater the divergence. Hence the necessity for some such hypothesis as that of complex-formation to account for the facts. Undoubtedly, it is the small but continually renewed amount of

adsorbed oxygen which forms the complex; as with all heterogeneous reactions, the reaction takes place in the condensed layer at the boundary between the two phases; but the complex-formation, and not the adsorption, is specific of the reaction between coal and oxygen.

It is, perhaps, necessary to answer the arguments brought forward in favour of the production of carbon dioxide through the agency of water-vapour, either from carbon monoxide or by direct action on the coal.

The suggested reactions are:  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ ;  $\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ ; and, possibly,  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ . Each of these reactions is known normally to proceed but slowly at temperatures below  $400^\circ$ . With the high concentration of the gases on the coal surface it is conceivable that they might be appreciable at  $100^\circ$  or lower. No such reactions occur during the oxidation of carbon at low temperatures, but, as already indicated, it is desirable not to stress the similarity between coal and carbon. Experiments were therefore made with coal, which showed:

(1) That no trace of hydrogen could be detected in oxygen which had been circulated over coal at  $100^\circ$  during several days.

(2) That (moist) mixtures of carbon monoxide and air circulated over coal at  $100^\circ$  suffered no change other than that due to the action of oxygen on the coal. No hydrogen was formed.

(3) That mixtures of hydrogen and air circulated over coal at  $100^\circ$  suffered no loss of hydrogen.

In each set of experiments the usual formation of carbon dioxide and carbon monoxide, in the ratio 2.4:1, took place.

Partington has suggested that "if the reaction between oxygen and coal were one of combination, with the formation of a complex oxide of carbon," the complex should have a definite univariant relationship between vapour pressure and temperature. The complex is not regarded as a definite oxide of carbon or of coal; there most probably are slightly differing compounds in coal to which the oxygen attaches itself, each forming a slightly different product. Probably, also, these oxygen-fixing compounds, which appear to be derived from the cellulosic portions of the original coal-forming materials, have no definite molecular dimensions, but are continuous in structure. The effect of progressive increase of temperature on the complex formed with oxygen by such compounds would be to cause progressive breakdown of their structure with elimination of the simple oxides, the residue requiring further increase in temperature to decompose it further.

## EXPERIMENTAL.

The results herein recorded were obtained during the course of an investigation which is still in progress (and, when completed, will form the subject of a communication to this Society), on the relative tendencies to spontaneous ignition of the several distinct portions into which a banded bituminous coal can be separated (see Stopes, *Proc. Roy. Soc.*, 1919, [B], 90, 470; Tideswell and Wheeler, this vol., 619). The particular coal used was the "durain" portion of the Thick Coal Seam, Hamstead Colliery.

The apparatus used, which will be described in detail when the complete research is described, enabled air or oxygen or any mixture of gases to be circulated in a closed system through the coal, which was packed in a reaction-tube the temperature of which could be maintained constant. The progress of the reaction could be followed by the change of pressure within the system and by analysis of the gases.

In all but the experiments with mixtures of carbon monoxide and air, in which a water-bubbler was used, the gases were dried by passage through a calcium chloride tube included in the circuit. The coal was ground so as to pass through a  $10 \times 10$  and remain on a  $60 \times 60$  mesh sieve. At the beginning and end of each experiment the coal, in position in the reaction tube, was raised to  $200^\circ$  and exhausted at that temperature.

Typical results for the absorption of pure oxygen at different temperatures are recorded in Fig. 1. Typical results when mixtures of carbon monoxide and air and hydrogen and air were used are as follow:

*Carbon Monoxide and Air (7.45 per cent. CO).*

Volume of apparatus: 3,300 c.c.

Mean pressure of gases: 660 mm.

Composition: Expressed as c.c. at  $15^\circ$  and 760 mm.

	CO <sub>2</sub>	O <sub>2</sub>	CO	N <sub>2</sub>	H <sub>2</sub>
Initial atmosphere.....	0.9	590	227	2240	nil
Final atmosphere (after circulation during 120 hours at $100^\circ$ ).....	53.4	79	249	2240	nil

Oxygen absorbed = 511 c.c. CO<sub>2</sub> formed = 52.5 c.c.

CO formed = 22 c.c. Ratio CO<sub>2</sub>/CO = 2.4.

	CO <sub>2</sub>	O <sub>2</sub>	CO	N <sub>2</sub>	H <sub>2</sub>
Gases removed from the coal by exhaustion at $200^\circ$ .....	26.5	nil	7.7	0.3	nil
Ratio CO <sub>2</sub> /CO removed at $200^\circ$ .....	3.3				



*Hydrogen and Air (3.85 per cent. H<sub>2</sub>).*

Volume of apparatus: 1,200 c.c.

Mean pressure of gases: 560 mm.

Composition: Expressed as c.c. at 15° and 760 mm.

	CO <sub>2</sub>	O <sub>2</sub>	CO	N <sub>2</sub>	H <sub>2</sub>
Initial atmosphere .....	nil	213.5	nil	788	40.2
After 20 hours at 100° ...	10.52	16.5	3.46	796	40.8
" 42 " " ...	11.20	4.9	4.60	791	39.7
" 66 " " ...	12.00	2.6	4.77	791	40.5

Oxygen absorbed = 211 c.c. CO<sub>2</sub> formed = 12.0 c.c.CO formed = 4.77 c.c. Ratio CO<sub>2</sub>/CO = 2.5.

	CO <sub>2</sub>	O <sub>2</sub>	CO	N <sub>2</sub>	H <sub>2</sub>
Gases removed from the coal by exhaustion at 200° .....	3.7	nil	1.2	0.1	nil
Ratio CO <sub>2</sub> /CO removed at 200° .....	3.1				

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LXXVI.—*The Catalytic Reduction of Hydrogen Cyanide.*

By SYDNEY BARRATT and ALAN FRANCIS TITLEY.

WHEN hydrogen cyanide vapour is reduced by gaseous hydrogen in the presence of metallic catalysts, mono-, di-, and tri-methylamine, ammonia, and methane form the bulk of the products. The present paper deals with the relative quantities of the basic substances produced, which were found to vary with the nature and temperature of the catalyst, and with other conditions which are described.

Debus (*Journ. Chem. Soc.*, 1863, **16**, 249) passed a mixture of hydrogen and hydrogen cyanide over platinum black and noticed reduction, accompanied by a considerable development of heat, even at the ordinary temperature. He states that the reaction proceeded vigorously at 110°, the main product being monomethylamine. The rapid decrease in the activity of the catalyst was attributed by him to the formation of a double cyanide of methylamine and platinum, which he isolated.

Linnemann (*Annalen*, 1868, **145**, 38), using the same catalyst, found that the reduction proceeded smoothly at 300°. Although the formation of the double salt was not observed, he found that the catalyst soon lost its activity.

Sabatier and Senderens (*Compt. rend.*, 1905, **140**, 482) investigated the reduction of hydrogen cyanide in the presence of nickel.

They showed that the temperature required for efficient reduction lay between  $300^{\circ}$  and  $400^{\circ}$ , or somewhat higher than that required by other nitriles. Ammonia and dimethylamine preponderated in the products isolated.

#### EXPERIMENTAL.

The larger number of the results described in this paper were obtained with platinum catalysts, but preliminary experiments were also carried out with finely divided iron prepared by the decomposition of ferrous oxalate at  $380^{\circ}$ .

With the latter catalyst, reduction proceeded at  $170^{\circ}$  and upwards. At  $200^{\circ}$ , the basic products isolated by passing the resulting gases through hydrochloric acid contained approximately 45 per cent. of monomethylamine and 55 per cent. of ammonia, with barely a trace of dimethylamine.

The rate of reduction was very low, even at higher temperatures, and after trials under varying conditions, the conclusion was reached that iron was an unsuitable catalyst for the reduction of hydrogen cyanide.

Platinum proved to be considerably more efficient than iron as a catalyst for this reduction, and although it was not found possible to employ the low temperatures suggested by Debus, the activity displayed by the platinum at rather higher temperatures was consistent throughout a long series of experiments.

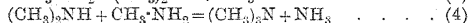
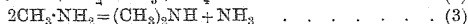
The catalyst was prepared by soaking blue asbestos fibre in platinum chloride solution. The resulting mass was then dried and reduced in a current of hydrogen at  $150^{\circ}$ . Catalysts containing from 0.1 to 40 per cent. of platinum on the asbestos were tested. Only those preparations containing more than 10 per cent. of platinum were of practical value in the form of apparatus described below. Those containing less platinum were not sufficiently vigorous, and the catalyst containing 20 per cent. of platinum was most frequently employed. Such variations in the composition of the catalyst affected only the efficiency of the reduction, and not the nature of the products.

Hydrogen cyanide dried by calcium chloride was prepared and liquefied, using the method described by Wade and Panting (T., 1898, 73, 255); its vapour, mixed with a regulated volume of electrolytic hydrogen, was passed through 22—30 cm. of platinised asbestos in a 1.3 cm. tube heated in a resistance furnace to a temperature measured by a thermo-couple. The alkaline products of the reduction were retained by passage of the gases through hydrochloric acid.

Under these conditions, reduction was first observed at 80°. The velocity of the reaction increases smoothly with rise of temperature to 180°, above which it was fairly rapid; for example, at 200°, 90—100 per cent. of the total hydrogen cyanide in a mixture, passed at the rate of 6 litres an hour, was reduced by 0.3 gram of platinum on 1 gram of asbestos. There appeared to be no advantage in raising the temperature of the catalyst above 220°. The composition of the products, however, was not appreciably affected by carrying out the reduction above 250°.

The products were analysed by the following method. The hydrochloric acid solution of the amines and ammonia was evaporated to dryness, and the solid chlorides were extracted with a known volume of absolute alcohol in excess over that required for complete solution of the amine hydrochlorides. Allowance being made for the slight solubility of ammonium chlorides in alcohol, evaporation of the alcoholic solution gave the total weight of amine hydrochlorides present. These were finally extracted with chloroform to separate the mono- and di-methylammonium chlorides.

From a consideration of the following equations,



it will be seen that, in accordance with the law of mass action, reaction (2) might be expected to be favoured by an excess of hydrogen in the gas mixture passing the catalyst. The very reverse, however, took place. If the partial pressure of the hydrogen cyanide was high and approached that required in theory for complete utilisation of the hydrogen (that is, 1 vol. of hydrogen cyanide to 2 vols. of hydrogen), then the products consisted almost entirely of ammonia. As the partial pressure of the hydrogen cyanide decreased, however, the proportion of the methylamines in the product rapidly increased. This continued up to a maximum, above which, however dilute a gas mixture was employed, the methylamine content of the product was constant. The following table and figure illustrate this point.

Composition of gas mixture.		Total methylamines, per cent.	Ammonia, per cent.
1 vol. HCN to 1½ vols. H₂.....		8	92
1 " " 4 " " .....		33	66
1 " " 6 " " .....		68	32
1 " " 8 " " .....		78	22
1 " " 15 " " .....		80	20

We are unable to offer an explanation of this anomaly.

The "total methylamines" given in the above table consist of mono- and di-methylamines in varying proportions, although trimethylamine is also present in minute quantities. The proportion between mono- and di-methylamine, as would be expected, is also affected by the partial pressure of hydrogen cyanide in the reacting gases. With a concentration of 1 vol. of hydrogen cyanide to 4 vols. of hydrogen, more than half of the total methylamine was dimethylamine. With 1 vol. of hydrogen cyanide to 15 vols. of hydrogen, this decreased to less than 10 per cent. of the total. This is shown in the accompanying figure (curve A).

Composition of gas mixture.	Mono- and di-methylamine in the products. Per cent.	
	Mono-	Di-
1 vol. HCN to 4.0 vols. H <sub>2</sub> ...	10	25
1 " " 4.4 " " ...	15	23
1 " " 5.6 " " ...	40	20
1 " " 6.3 " " ...	54	16
1 " " 8.0 " " ...	66	12
1 " " 15.0 " " ...	72	8

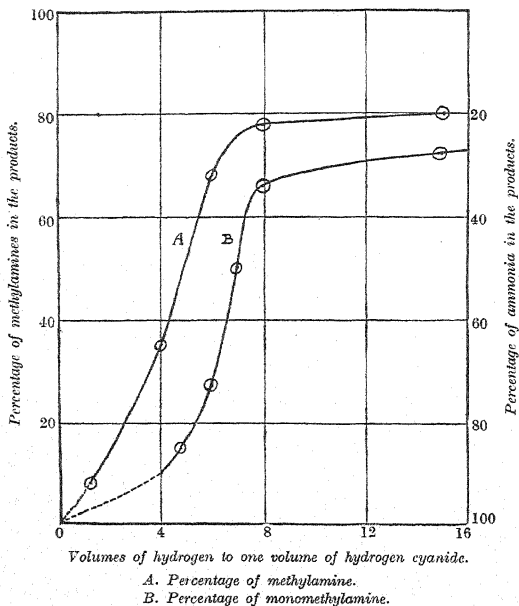
The figures given in the tables above vary within about 5 per cent. in individual experiments, made with different preparations of catalyst containing the same amount of platinum. The tables represent the results obtained with a catalyst prepared as described, and working at temperatures from 180° to 220°.

The alteration in the behaviour of the catalyst with use proved to be unusual. Although the formation of a double cyanide of platinum and methylamine, to which Debus attributed the short-lived activity of his platinum black, was never observed, the activity of our catalysts was found to undergo a peculiar change during successive experiments. The longer the time in use, in spite of identical conditions of temperature and gas concentration, the greater the percentage of ammonia in the reduction products became. This change was very irregular, but occurred more rapidly the less platinum there was on the asbestos. Thus with 0.4 gram of platinum deposited on 1 gram of asbestos, the composition of the products was constant during a period of fifteen hours, but with only 0.1 gram of platinum to the same weight of asbestos, an appreciable difference was noticed after one hour.

Attempts to renew the original behaviour of the catalyst by heating in hydrogen, oxygen, or hydrogen chloride up to 600° were unsuccessful. Treatment with chlorine, however, at 200° for a short period completely renewed the former activity, and, in one or two cases, brought about a slight increase in the yield of methyl-

amine over that obtained with the freshly prepared platinum. In one case, the original percentage of methylamines in the products was 79; during five hours' use of the same catalyst, this decreased to 50, but, after passage of chlorine over the platinum, rose to 86 at the same temperature and with the same concentration of the gases.

*Graph illustrating the changes in the products of reduction caused by alterations in the composition of the gas mixture.*



At the close of the above work, the conditions were briefly studied, under which methylamine decomposes into hydrogen and hydrogen cyanide.

Liquid monomethylamine was prepared from the hydrochloride and sodium hydroxide, and its vapour passed over a platinum catalyst, prepared as described. It was found that the dehydrogen-

ation, although perceptible at  $220^{\circ}$ , only proceeds with considerable velocity above  $300^{\circ}$ , that is, at temperatures more than  $100^{\circ}$  higher than the minimum required for efficient hydrogenation of the cyanide. This is in accordance with the general rule observed by Sabatier.

Since ammonia and methane, as well as hydrogen cyanide and dimethylamine, were detected in the products, it appears probable that the hydrogen resulting from the dehydrogenation process reduces a further portion of the methylamine (compare Sabatier and Mailhe, *Compt. rend.*, 1917, **165**, 224, 309).

#### *Summary.*

(1) Platinum catalyses the reduction of hydrogen cyanide by gaseous hydrogen above  $120^{\circ}$ , readily above  $180^{\circ}$ .

(2) The nature of the reduction products, although unaffected by alterations of temperature between  $120^{\circ}$  and  $250^{\circ}$ , is dependent on the partial pressure of the hydrogen cyanide in the gas mixture employed, the proportion of monomethylamine increasing to a maximum as this partial pressure is decreased. The secondary reactions which give rise to di- and tri-methylamine are also less marked the lower the pressure of the hydrogen cyanide.

If the concentration of the hydrogen cyanide in the gas mixture is made sufficiently small, a yield of 80 per cent. of total methylamines, and more than 70 per cent. of monomethylamine, can be obtained.

(3) On continued use of a given catalyst, the yield of methylamine diminishes, and is replaced by ammonia. The original behaviour of the platinum is restored by treatment with chlorine.

(4) The dehydrogenation and auto-reduction of methylamine only proceeds with noticeable velocity above  $300^{\circ}$  in the presence of platinum, and was not observed at  $200^{\circ}$ , the temperature employed in the majority of the experiments described in this communication.

Our thanks are due to Professor F. Francis for the assistance he gave us during this investigation.

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[Received, June 12th, 1919.]

LXXVII.—*The Chemistry of Burgundy Mixtures.*

By ROBERT LUDWIG MOND and CHRISTIAN HEBERLEIN.

ALTHOUGH mixtures of sodium carbonate and copper sulphate, generally known as "Burgundy mixtures," have been in use for a number of years as a most effective agent for combating plant diseases of a fungoid character, the chemical reactions which take place when these substances are mixed in solution have hitherto not received much attention.

Abegg ("Handbuch der anorg. Chemie," II., i, 633) states: "From solutions of copper sulphate, sodium carbonate at ordinary temperatures gives a greenish-blue colloidal precipitate of varying composition, which contains absorbed alkali carbonate. With excess of copper sulphate the precipitate also contains basic copper sulphate. With equivalent quantities of the components the gel contains copper and carbon dioxide in the ratio  $2\text{CuO} : 1\text{CO}_2$ ."

If the precipitates are left with the mother liquor they become crystalline and change into the green, granular basic carbonate,  $3\text{CuCO}_3 \cdot 3\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ .

In contact with a concentrated solution of sodium carbonate, the gel is transformed into Deville's blue, crystalline double carbonate,  $\text{Na}_2\text{CO}_3 \cdot \text{CuCO}_3 \cdot 3\text{H}_2\text{O}$ ."

This statement pointed to a complexity of reactions which required further elucidation. The fact that a colloidal solution was formed appeared to us to have an important bearing on the fungicidal properties of the material in question, and we asked Prof. Barker, of the University of Bristol, to investigate the relative advantages of the colloidal over the crystalline state. His preliminary results are embodied in a very interesting paper, which will be published in the University's Annual Report.

In spite of the highly significant work which has been done by Pickering (T., 1909, 95, 1409) and Ravaz ("Le Mildion," Paris, Masson and Cie., 1914) on Burgundy mixture, we found the problem more complicated than they had assumed, and we proceeded to carry out our investigations on the following lines:

(1) The main reactions between copper sulphate and sodium carbonate were quantitatively studied with various ratios of the components.

(2) The reaction between copper sulphate and sodium hydrogen carbonate was examined.

(3) The free carbon dioxide and the carbon dioxide in the precipitate were estimated, and the ratio  $\text{CuO}:\text{CO}_2$  in the precipitate was determined.

(4) The solvent action of carbonic acid was studied.

(5) The basic sulphate was determined in various mixtures to ascertain the ratio  $\text{CuO}:\text{SO}_3$  and  $\text{CuO}:\text{CO}_2:\text{SO}_3$ .

(6) The absorbed sodium carbonate was estimated.

(7) The causes and reactions of the change from the colloidal precipitate to malachite were investigated.

(1) *The Main Reactions between Copper Sulphate and Sodium Carbonate.*

The mixtures were generally made at  $15^\circ$  by dissolving 4 grams of crystallised copper sulphate in 200 c.c. of water and a varying amount of crystallised sodium carbonate in 200 c.c. of water, and then pouring the two solutions simultaneously into a third beaker, thus avoiding any excess of one reagent over the other. The mixtures were tested (a) with litmus paper; (b) the copper in solution was estimated by electrolysis; (c) a filtered portion of the mixture was tested directly with ferrocyanide; (d) a filtered portion, after boiling and filtering, was tested with ferrocyanide; (e) the free sodium hydrogen carbonate and the basic copper sulphate in solution were titrated with  $N/10$ -hydrochloric acid, using methyl-orange as indicator; (f) the free sodium carbonate was titrated with phenolphthalein as indicator.

The various mixtures and the results of the analyses are tabulated in table I.

It will be noticed that a theoretical mixture of equivalent amounts of copper sulphate and sodium carbonate, namely, 4 grams of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} : 4.58$  grams of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , although reacting alkaline towards litmus and methyl-orange, contains a considerable amount of copper in solution. A mixture with 7.38 grams of sodium carbonate (Pickering's mixture) contains the minimum amount of soluble copper. Larger amounts of sodium carbonate cause the formation of complex compounds containing electronegative copper.

From curve 1 in Fig. 2 it will be seen that the solution is alkaline towards methyl-orange after a small addition of sodium carbonate, due to soluble basic copper sulphate. The curves in this figure show three distinct stages. Up to 4.25 grams of sodium carbonate the solution contains free copper sulphate and an increasing amount



TABLE I.

Copper sulphate. Grams.	Crystalline sodium carbonate. Grams.	Molecular ratio, $\text{CuSO}_4 : \text{Na}_2\text{CO}_3$	Litmus reaction.	After filtration.	After boiling.	Grams per litre.	Per cent. on total.	Titration with N/10-HCl.		In solution in total mixture.	Percentage in solution on total carbonate used, = 100 per cent.		
								C.c.	C.c.		as $\text{Na}_2\text{CO}_3$ .	as $\text{NaHCO}_3$ .	as $\text{NaHCO}_3$ .
4.0	2.13	1:0.46	acid	Cu	Cu	1.240	50.22	0.22	—	—	—	—	—
4.0	3.18	1:0.70	"	"	"	0.72	29.16	0.38	—	—	—	—	—
4.0	4.15	—	neutral	"	"	—	—	0.59	—	0.1982	—	7.9	7.9
4.0	4.20	—	"	"	trace	—	—	0.68	—	0.2413	—	9.7	9.7
4.0	4.25	1:0.93	"	"	Cu	0.24	9.6	0.64	—	0.2150	—	8.6	8.6
4.0	4.50	1:0.98	faintly alkaline	"	"	0.20	8.0	0.81	—	0.2045	—	10.0	10.0
4.0	5.0	1:1.10	"	"	"	0.12	4.8	1.29	—	0.4389	—	14.9	14.9
4.0	6.38	1:1.39	"	"	"	0.04	1.6	3.12	—	1.080	—	28.8	28.8
4.0	7.38	1:1.62	"	trace Cu	"	0.005	0.2	4.63	—	1.5946	—	36.8	36.8
4.0	7.45	—	distinctly alkaline	"	"	—	—	4.54	—	—	—	—	—
4.0	7.52	—	"	"	"	—	—	0.10	4.57	—	—	—	—
4.0	7.59	—	"	"	"	—	—	0.15	—	—	—	—	—
4.0	7.66	—	"	"	"	—	—	0.15	4.75	—	—	—	—
4.0	7.94	—	strongly alkaline	"	"	—	—	0.43	4.84	—	—	—	—
4.0	8.5	1:1.86	"	"	"	0.01	0.4	1.54	4.84	0.3347	10.6	31.6	42.2
4.0	12.75	1:2.79	"	Cu	Cu	0.02	0.8	7.81	5.46	1.6971	35.9	25.1	61.0

(standard  
mixture.

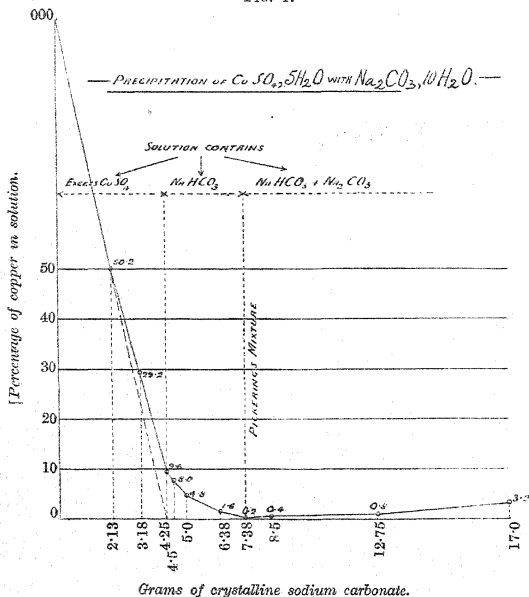
TABLE I (continued).

Copper sulphate.	Crystalline sodium carbonate.	Grams.	Molecular ratio. $\text{CuSO}_4 : \text{Na}_2\text{CO}_3$ .	Litmus reaction.	After filtration.	After boiling.	Potassium ferriocyanide.		Copper in solution.		Titration with $\text{N}/10\text{-HCl}$ .		In solution in total mixture.		Percentage in solution on total carbonate used, = 100 per cent.		
							Grams per litre.	Per cent. on total.	C.c. for $\text{Na}_2\text{CO}_3$ .	C.c. for $\text{NaHCO}_3$ .	Grams $\text{Na}_2\text{CO}_3$ .	Grams $\text{NaHCO}_3$ .	Grams $\text{Na}_2\text{CO}_3$ .	Grams $\text{NaHCO}_3$ .	as $\text{Na}_2\text{CO}_3$ .	as $\text{NaHCO}_3$ .	as $\text{NaHCO}_3$ .
4.0	4.0	4.25	1 : 3.72	strongly alkaline.	Cu	Cu	0.08	3.2	13.90	6.19	3.0400	2.1318	48.2	21.3	69.5	7.9	7.9
4.0	4.0	4.25	1 : 0.93	—	—	—	0.22	—	—	0.58	—	0.1973	—	7.9	—	7.9	—
—	—	—	—	—	—	—	0.36	—	—	1.11	—	0.3776	—	15.1	—	15.1	—
—	—	—	—	—	—	—	0.42	—	—	1.18	—	—	—	—	—	—	—
4.0	4.0	4.25	1 : 0.93	—	—	—	0.02	—	—	0.10	—	—	—	—	—	—	—
4.0	4.0	4.25	1 : 0.93	—	—	—	0.04	—	—	0.10	—	—	—	—	—	—	—
4.0	4.0	4.25	1 : 0.93	—	—	—	nil	—	—	0.25	—	—	—	—	—	—	—
4.0	4.0	4.25	—	—	—	—	0.36	—	—	0.98	—	0.0370	—	1.6	—	1.6	—
4.0	4.0	4.5	—	—	—	—	0.20	—	—	1.22	—	0.1008	—	3.8	—	3.8	—
4.0	4.0	5.0	—	—	—	—	0.12	—	—	2.04	—	0.5715	—	19.5	—	19.5	—

of dissolved basic copper sulphate. From 4.25 to 7.38 grams the dissolved basic copper sulphate falls to a minimum. The sodium hydrogen carbonate rises regularly from nil, and beyond 7.38 grams of sodium carbonate free sodium carbonate appears.

Copper sulphate solution, as is well known, has an acid reaction, due to its tendency to form basic salts by hydrolysis. If the free

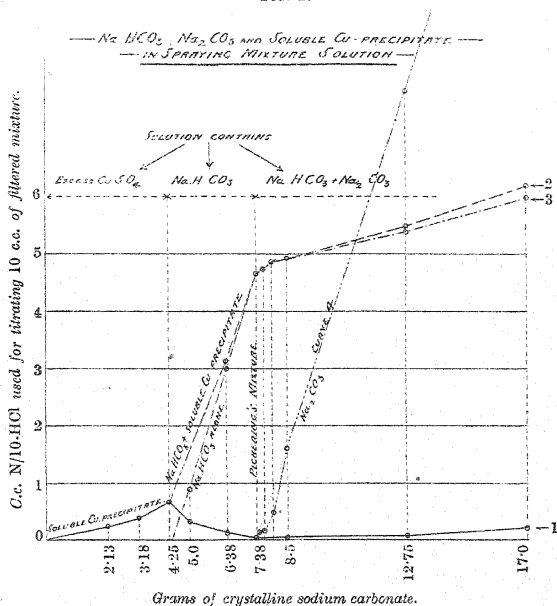
FIG. 1.



acid is neutralised by sodium carbonate, the solution will remain neutral or alkaline so long as the basic sulphate is kept in solution by the carbon dioxide evolved. With the gradual loss of the latter, the basic sulphate becomes insoluble, and further hydrolysis takes place until the solution is again acid. Further addition of sodium carbonate neutralises this acid, carbon dioxide is evolved, part of the

basic sulphate is precipitated, part of it is retained in solution by the carbon dioxide, and all these reactions are repeated until the whole of the copper sulphate is converted. The formation of basic copper sulphate is thus simply explained, and it is clear that a temporarily neutral solution can be obtained with very little sodium carbonate. A permanently neutral solution is obtained with 4.25

FIG. 2.



grams of sodium carbonate, which is less than the theoretical amount, because hydrolysis performs its share in the precipitation.

The sodium carbonate, besides neutralising the free acid, acts on the basic sulphate, converting it partly into basic carbonate. The carbon dioxide thus evolved increases the solubility of the basic sulphate, and with 4.25 grams of sodium carbonate the maximum

amount of free carbon dioxide and of dissolved basic sulphate is reached. Above 4.25 grams the excess of sodium carbonate is converted into hydrogen carbonate, the amount of carbon dioxide decreases, and proportionate amounts of basic sulphate are precipitated. At 7.38 grams of sodium carbonate all carbon dioxide has disappeared and the minimum of dissolved basic copper sulphate is reached. Above 7.38 grams the solution contains also normal carbonate, which forms soluble complex copper compounds, as is shown in the rising curve of soluble copper.

We have therefore established that the complete conversion of 4 grams of crystallised copper sulphate is effected with 4.25 grams of crystallised sodium carbonate, that is, 92.8 per cent. of the theoretical quantity. Such a mixture reacts neutral towards red litmus paper, faintly acid towards blue litmus (owing to the free carbon dioxide), and alkaline towards methyl-orange. If the mixture is filtered, the filtrate, which will contain 9.6 per cent. of the total copper as soluble basic sulphate, gives a heavy, red precipitate with ferrocyanide. This is due to the secondary action of the carbon dioxide, and the test is therefore misleading. If, however, the carbon dioxide is eliminated, either by a current of air or by boiling, and then the ferrocyanide test applied, no trace of copper can be detected in solution.

As this mixture of copper sulphate and sodium carbonate contains no free copper sulphate and no free alkali, carbonate or hydrogen carbonate, but, on the other hand, the maximum of dissolved basic copper sulphate, it may be regarded as having not only the highest fungicidal efficiency, but also a maximum potentiality to cause injury to foliage. This is borne out by Prof. Barker's experiments, and in the field.

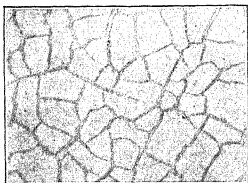
Physical examination of our mixture showed that the copper precipitate, as well as the dissolved basic sulphate, is in the colloidal condition. The sodium sulphate mother liquor can be separated from the dissolved basic sulphate by dialysis. On removal of the carbon dioxide the hydrosol of basic copper sulphate separates as well, the reaction being easily reversible.

As is well known, Burgundy mixture changes after a while from a colloidal into a crystalline condition, giving rise to a number of chemical reactions which will be examined hereafter.

The addition of 0.02 per cent. of glue was found to be most effective in prolonging the period during which the colloidal state exists.

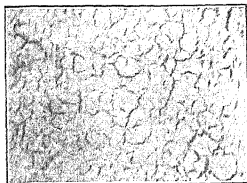
The three micro-photographs illustrate the drying of a colloidal film; (a) is without glue; (b) with glue; and (c) is without glue,

*Colloidal*  
(A) *Without glue.*



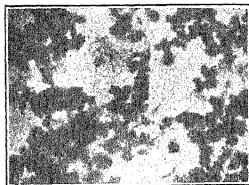
*Magnified*

*Colloidal.*  
(B) *With glue.*



*Magnified.*

*Crystalline.*  
(C) *Without glue*



*Magnified.*



showing the change to the crystalline state. The separate crystals of malachite and sodium sulphate are clearly distinguishable.

(2) *The Reaction between Copper Sulphate and Sodium Hydrogen Carbonate.*

We found that the reaction between copper sulphate and sodium hydrogen carbonate proceeds similarly to the case of the normal carbonate; basic sulphate and basic carbonate are formed, carbon dioxide is set free, and a similar amount of basic sulphate is dissolved. The minimum weight of sodium hydrogen carbonate for complete conversion is 2.50 grams or 92.6 per cent. of the theoretical. This figure is close to the figure 92.8 found for the normal carbonate, and here also the hydrogen carbonate acts not as a direct precipitating agent, but as a neutralising agent. The copper precipitate obtained with the hydrogen carbonate has a paler blue colour, it separates out sooner from the mother liquor, being less hydrated, and contains  $\text{Cu} = 21.02$ ;  $\text{CO}_2 = 5.67$  per cent., and has a ratio  $\text{CuO}:\text{CO}_2 = 2.56:1$ .

(3) *Estimation of Carbon Dioxide in the Copper Precipitate, and of the Free Carbon Dioxide.*

TABLE II.

			Carbon dioxide evolved, per cent.	Percentage of carbon dioxide on total carbon dioxide. = 100 per cent.
Crystalline sodium carbonate plus sulphuric acid ... ..	on boiling		15.1	100
4 grams of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ + 4.25 grams of crystalline sodium carbonate ... ..	15°	} Average = 52.4	7.87	
" "	"		7.95	
" "	60°		9.78	64.8
" "	on boiling		15.10	100.0



TABLE III.  
*Showing the Molecular Ratio CuO:CO<sub>2</sub> in the Precipitate.*

No.	Mixture.	After.	Percentage in precipitate		Mol. ratio.	
			CuO.	CO <sub>2</sub>	CuO : CO <sub>2</sub>	
1	4 grams of CuSO <sub>4</sub> .5H <sub>2</sub> O + 4.25 grams of Na <sub>2</sub> CO <sub>3</sub> .10H <sub>2</sub> O	colloid.	5.10	1.56	2.26 : 1	
2	"	$\frac{1}{2}$ hour.	6.10	1.85	2.28 : 1	Filtered, not washed.
3	"	1 day.	6.10	1.68	2.51 : 1	
4	"	1½ days.	6.10	1.53	2.76 : 1	
5	"	2 "	7.91	2.43	2.25 : 1	Filtered and washed twice.
6	"	$\frac{1}{2}$ hour.	7.91	2.32	2.36 : 1	
7	"	3 hours.	7.91	2.26	2.42 : 1	
8	4 grams of CuSO <sub>4</sub> .5H <sub>2</sub> O + 4.25 grams of Na <sub>2</sub> CO <sub>3</sub> .10H <sub>2</sub> O and glue	1 hour	7.67	2.42	2.19 : 1	Washed.
9	"	36 days.	6.76	1.35	3.46 : 1	"
10	4 grams of CuSO <sub>4</sub> .5H <sub>2</sub> O + 7.38 grams of Na <sub>2</sub> CO <sub>3</sub> .10H <sub>2</sub> O	1 hour.	7.54	2.36	2.21 : 1	"
11	4 grams of CuSO <sub>4</sub> .5H <sub>2</sub> O + 2.125 grams of Na <sub>2</sub> CO <sub>3</sub> .10H <sub>2</sub> O	"	4.20	1.26	2.30 : 1	"
12	4 grams of CuSO <sub>4</sub> .5H <sub>2</sub> O + 1.0625 grams of Na <sub>2</sub> CO <sub>3</sub> .10H <sub>2</sub> O	"	4.68	0.42	7.7 : 1	"

TABLE III (continued).

Showing the Molecular Ratio  $\text{CuO} : \text{CO}_2$  in the Precipitate.

No.	Mixture.	After.		Percentage in precipitate		Mol. ratio.	
				CuO.	CO <sub>2</sub> .	$\frac{\text{CuO}}{\text{CO}_2}$	$\frac{\text{CuO}}{\text{CO}_2}$
13	4 grams of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ + 4.25 grams of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ at 60°	1 hour	crystalline	—	—	2.93 : 1	
14	4 grams of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ + 4.25 grams of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ at 80°	"	"	8.99	0.83	7.5 : 1	
15	4 grams of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ + 4.25 grams of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ at 15°	7 days.	"	31.89	7.51	2.94 : 1	
16	4 grams of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ + 4.25 grams of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	4 "	"	15.96	2.88	3.84 : 1	Sprayed on glass and dried.
17	"	22 "	"	47.89	8.38	3.97 : 1	
18	"	8 "	"	11.35	3.06	2.57 : 1	
19	"	7 "	"	23.65	5.08	3.22 : 1	Filtered, washed, and stirred with water. Passing air through for 2 hours. Left until crystalline.
20	"	7 "	"	19.53	3.79	3.56 : 1	
21	"	18 "	"	33.5	11.9	1.95 : 1	
22	"	5 "	"	23.8	8.39	1.99 : 1	In stoppered bottle. Saturated CO <sub>2</sub> .
23	"	5 "	"	27.3	9.46	2.00 : 1	
24	"	1½ "	"	24.58	4.14	4.11 : 1	
25	4 grams of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ + 2.45 grams of $\text{NaHCO}_3$	1 hour.	colloid	21.02	5.67	2.56 : 1	Filtered, stirred with $\text{NaHCO}_3$ solution.

The average ratio in a 4.25 mixture is  $\text{CuO}:\text{CO}_2=2.25:1$ . Experiments 1 to 7 show that the copper precipitate, when formed, quickly loses carbon dioxide, the ratio altering gradually. On keeping the mixture in an open vessel, carbon dioxide is liberated by the decomposition of the basic copper carbonate and the precipitate becomes crystalline. It is not yet evident, however, from these experiments that the change of the colloidal to the crystalline state is due to any alteration of the ratio  $\text{CuO}:\text{CO}_2$ .

Fresh colloidal mixtures have the ratio  $\text{CuO}:\text{CO}_2=2.26:1$ .

Old crystalline mixtures have the ratio  $\text{CuO}:\text{CO}_2=2.94:1$ .

Old crystalline mixtures saturated with carbon dioxide  $=2.00:1$ .

Old colloidal mixtures and glue have the ratio  $\text{CuO}:\text{CO}_2=2.46:1$ .

#### (4) *The Solvent Action of Carbonic Acid.*

An examination of the constitution of the dissolved basic copper compound present in acid, neutral, and alkaline mixtures has proved to us that only basic copper sulphate is dissolved by the carbon dioxide. Reference to curve 1 in Fig. 2 shows that the amount of copper precipitate dissolved by carbon dioxide rises gradually to a maximum containing 4.25 grams of sodium carbonate, then falls to its lowest point at 7.38. This maximum of dissolved copper corresponds with 9.6 per cent. of the total copper and is equal to 0.24 gram of copper per litre in a 1 per cent. mixture. By saturat-

TABLE IV.

Time.	Mixture 1 without glue. Soluble copper per litre.	Mixture 2 with glue. Soluble copper per litre.
	Gram.	Gram.
After mixing .....	0.26	0.30
1 hour .....	—	0.22
2 hours .....	0.22	—
4 " .....	0.22	—
1 day .....	0.22	0.22
2 days .....	0.22	—
3 " .....	0.22	—
5 " .....	0.16	—
6 " .....	—	0.16
7 " .....	0.10	—
	(precipitate begins to change)	
9 " .....	0.06	0.10
10 " .....	0.06	—
11 " .....	0.06	0.10
13 " .....	0.02	0.10
14 " .....	0.00	—
16 " .....	—	0.06
20 " .....	—	0.02
22 " .....	—	0.01
24 " .....	—	nil

ing such a mixture with carbon dioxide the amount of soluble copper can be raised to 0.36 gram per litre. On the other hand, a mixture of 4 grams of crystallised copper sulphate and 8.5 grams of crystallised sodium carbonate containing 0.04 gram of copper per litre on being saturated with carbon dioxide shows scarcely any more soluble copper (0.06 gram per litre). The amount of basic copper sulphate in such a mixture being very small, the carbon dioxide finds little to dissolve, thus affording further proof that the copper carbonate is not dissolved by the carbon dioxide.

If an ordinary mixture, containing 4.25 grams of crystalline sodium carbonate, is allowed to remain in an open vessel, carbon dioxide is gradually evolved, and the amount of dissolved basic copper sulphate decreases in proportion. Table IV (p. 918) illustrates this.

After fourteen days an ordinary mixture containing 4.25 grams of crystalline sodium carbonate shows no more soluble copper and the precipitate has all turned to malachite. A similar mixture with 0.02 per cent. of glue loses its soluble copper more slowly, and after twenty-four days is still blue and colloidal.

(5) *The Basic Sulphate in the Copper Precipitate.*

TABLE V.

Mixture.		Sulphur in precipitate on total sulphur in mixture, =100 per cent.	Copper precipitated. Per cent.	Molecular ratio, CuO : SO <sub>3</sub> .
CuSO <sub>4</sub> , 5H <sub>2</sub> O	Na <sub>2</sub> CO <sub>3</sub> , 10H <sub>2</sub> O.			
4	0.2688	2.10	6.25	2.8 : 1
4	0.5375	3.7	12.5	3.2 : 1
4	1.075	6.9	25.0	3.5 : 1
4	2.15	14.7	50.0	3.2 : 1
4	3.2256	22.4	75.0	3.3 : 1
4	3.7632	21.5	87.5	4.0 : 1
4	4.0320	17.1	93.75	5.3 : 1
4	4.30	6.3	100.0	15.0 : 1
4	5.375	4.3	100.0	22.4 : 1
4	5.45	3.2	100.0	30.9 : 1
4	8.60	0.75	100.0	126.0 : 1
4	4.30	10.10	100.0	9.6 : 1

(precipitated at 80°)

Basic sulphate is found in every mixture. With small amounts of sodium carbonate, more basic sulphate is found than basic carbonate. With an increasing amount of sodium carbonate the ratio CuO:SO<sub>3</sub> keeps fairly constant for a time. The ratio in our mixture is 15:1. Whereas the ratio CuO:CO<sub>2</sub> shows little difference in varying mixtures, the ratio CuO:SO<sub>3</sub> alters greatly in mixtures containing an excessive amount of sodium carbonate, and the SO<sub>3</sub>

disappears almost completely in a mixture containing 8.6 grams of sodium carbonate.

Treatment with saturated aqueous carbon dioxide decreases the  $\text{SO}_3$  in the precipitate, and sodium hydrogen carbonate dissolves the  $\text{SO}_3$  completely.

The ratio  $\text{CuO} : \text{SO}_3$  in the soluble basic copper sulphate was found to be 3.5 : 1.

(6) *Estimation of the Absorbed Sodium Carbonate in the Copper Precipitate.*

On examining the titration figures in table I it will be noticed that the amount of sodium carbonate and hydrogen carbonate found in solution of the mixtures with an excessive amount of sodium carbonate ranges from 4.5 to 7.8 per cent. below the amount calculated. This can only be accounted for by its being absorbed by the precipitate. A direct estimation of the alkali in the precipitate was made and the above figures were confirmed.

TABLE VI.

Mixture	$\text{Na}_2\text{CO}_3$ in precipitate on total soda used, = 100 per cent.	Mol. ratio $\text{CuO} : \text{Na}_2\text{CO}_3$ in precipitate.
4 grams of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ + 4.25 grams of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ...	4.0	73.5 : 1
4 grams of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ + 4.25 grams of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ with glue	4.1	75.3 : 1
4 grams of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ + 8.5 grams of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ...	6.8	44.4 : 1

(7) *Causes of the Change from the Colloid to Malachite.*

Our experiments suggest that the colloidal state of the precipitate is dependent on the presence therein of sodium carbonate. The absorbed alkali is given up after some time and passes into solution, wherein it can be titrated.\* The presence of an excessive amount of sodium carbonate in solution prevents this; a copper precipitate washed completely and stirred with sodium carbonate solution maintains its colloidal state indefinitely.

For the same reasons spraying mixtures with free sodium carbonate in solution (mixtures with more than 7.38 grams of sodium carbonate) retain the colloidal condition. Glue seems to act in a similar protective way.

Free carbon dioxide and sodium hydrogen carbonate destroy the

\* When the maximum amount of free alkali in solution is reached, the change of the colloidal precipitate to the crystalline begins to be visible.

colloidal compound, the former acting on the absorbed sodium carbonate, forming hydrogen carbonate, the latter acting on the  $\text{SO}_3$  groups, thus decomposing the compound.

A mixture containing 4.25 grams of crystallised sodium carbonate kept in an open vessel at  $15^\circ$  changes to malachite in seven days. Acid mixtures with less sodium carbonate or alkaline mixtures with less than 7.38 grams of sodium carbonate change sooner.

The presence of glue in every case retards the change.

### *Conclusions.*

(1) On mixing copper sulphate with sodium carbonate solution three distinct copper compounds are formed: (a) Insoluble hydrated basic copper carbonate, which forms the bulk of the precipitate; (b) insoluble hydrated basic copper sulphate; and (c) soluble basic copper sulphate. Complete conversion of copper sulphate into these salts is obtained when for 1 molecule of copper sulphate 0.93 molecule of sodium carbonate is added, or for 4 grams of crystallised copper sulphate, 4.25 grams of crystallised sodium carbonate ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ).

(2) Judging by the results obtained, there appears to be no well-defined compound of copper, the composition altering according to conditions of precipitation. All the copper compounds are subject to rapid changes, the basic copper carbonate losing carbon dioxide and the dissolved basic copper sulphate soon becoming insoluble.

(3) A 1 per cent. mixture of 4 grams of copper sulphate and 4.25 grams of crystallised sodium carbonate made at  $15^\circ$  gives

(a) Basic copper carbonate containing  $\text{CuO}$  and  $\text{CO}_2$  in the ratio 2.2:1.

(b) Insoluble basic copper sulphate containing  $\text{CuO}$  and  $\text{SO}_3$  in the ratio 15:1.

(c) Soluble basic copper sulphate equal to 9.6 per cent. of the total copper present.

(4) On making the mixture at  $15^\circ$  free carbon dioxide is evolved, equal to 52.4 per cent. of the total carbon dioxide present in the sodium carbonate.

(5) At a higher temperature more carbon dioxide is evolved, until on reaching boiling point all carbon dioxide is expelled and the copper precipitate is converted into black copper hydroxide.

(6) The amount of basic copper sulphate formed is dependent on the amount of sodium carbonate used, and decreases as the latter is increased.

(7) The free carbon dioxide acts as a solvent on the basic copper sulphate only, not on the basic copper carbonate.

(8) The maximum of soluble basic copper sulphate is obtained in a mixture of 4 grams of copper sulphate and 4.45 grams of crystallised sodium carbonate for the reason that this mixture gives the maximum of free carbon dioxide.

(9) With larger amounts of sodium carbonate free carbon dioxide is neutralised to form sodium hydrogen carbonate.

(10) A mixture with 7.38 grams of crystallised sodium carbonate contains no more free carbon dioxide, and therefore a minimum of soluble basic copper sulphate.

(11) The copper precipitate at  $15^{\circ}$  contains absorbed sodium carbonate in the ratio  $\text{CuO}:\text{Na}_2\text{CO}_3=74:1$ .

(12) The whole of the copper precipitate is at first colloidal. After a short or long period, according to the temperature and the ratio of the ingredients in the mixture, the gel changes to the crystalline state.

(13) Addition of 0.02 per cent. of glue prolongs the life of the gel.

(14) Presence of free copper sulphate, or sodium hydrogen carbonate, or carbonic acid in the mixture accelerates the change of the colloidal to the crystalline state, whereas normal sodium carbonate helps to maintain the colloidal condition.

(15) The dissolved basic copper sulphate is in the form of hydrosol.

(16) The colloidal state of the precipitate appears to be conditional on the absorbed sodium carbonate.

(17) This absorbed sodium carbonate is found in the solution after some time, whereupon the change of the colloid to the crystalline begins to be visible.

(18) Changes in the sulphur content of the copper precipitate also take place during the change of the colloid to the crystalloid.

(19) The crystalline precipitate contains less carbon dioxide than the colloid. The ratio of  $\text{CuO}:\text{CO}_2$  in old crystalline precipitate is found to be 2.94:1.

From the results obtained in this research it is apparent that the chemistry of "Burgundy mixture" is of a much more complex nature than previously suspected, and there are a number of questions which have to be further elucidated. The nature of the colloid solution and the conditions of its formation and change to the crystalline state await further investigations, and the influence produced by small quantities of glue indicates the importance of making further experiments with similar colloids.

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# LXXVIII.—*Examination of the Bark of Croton gubouga.* *Isolation of 4-Hydroxyhygric Acid.*

By JOHN AUGUSTUS GOODSON and HUBERT WILLIAM BENTLEY  
 CLEWER.

*Croton gubouga*, S. Moore, is a small tree growing on the low veldt in the Eastern Transvaal near the Sabi and Selati rivers. The bark of the tree has a considerable local reputation among the natives as a remedy for malaria, and both the seeds and the bark have been used by Captain Maberley in conjunction with opium in the treatment of malarial fever (*Lancet*, 1899, 157, 874).

A preliminary examination of the bark and the seeds has been made by Mr. H. H. Green, B.Sc., in South Africa (private communication), who found that the ground bark caused purgation and emesis in dogs, but that rabbits were less sensitive to its action, although in doses of 1 gram per kilogram of body-weight it induced diarrhœa. In human beings administration of the bark according to Mr. Green causes an intense burning sensation in the throat, salivation, and slight nausea, with, in some cases, a slight laxative effect. The seeds exert a similar action. Mr. Green further observed that the acrid substance to which these effects are ascribed is extracted to some extent by hot water, and readily by ether.

The bark has also been examined by Greenish (*Pharm. J.*, 1918, 101, 289), who found that the acrid constituent was largely extracted by hot light petroleum as well as by ether, chloroform, or alcohol.

For the material used in the present investigation the authors are indebted to Mr. I. B. Pole Evans, Chief of the Division of Botany, Union of South Africa.

The bark had a slight but not unpleasant odour. Dust from the ground bark caused sneezing and produced a burning sensation in the throat and on the tongue. It has not been possible to isolate the acrid constituent to which the irritant properties of the bark are due, in a form suitable for investigation, and it is possible that the seeds, which it is hoped to examine shortly, may prove more suitable for this purpose. The present paper deals chiefly with an acid isolated from the bark, which has proved to be a new optically active hydroxyhygric acid.



*Preliminary Examination.*

When extracted with Prollius' fluid the ground bark yielded a trace of alkaloid and furnished the following percentages of extract when exhausted in a Soxhlet apparatus with solvents in the order named: petroleum (b. p. 35—60°), 3; ether, 0·7; chloroform, 0·3; ethyl acetate, 0·8; alcohol, 4·3; total, 9·1.

*Petroleum Extract.*—This extract, on treatment with ether, left only a trace of insoluble matter. The solution yielded only traces of material to aqueous solutions of ammonium and potassium carbonates, but potassium hydroxide solution extracted a quantity of brown potassium salt, from which fatty acids (A), equivalent to 21 per cent. of the original extract, were recovered.

The solution left after the removal of the fatty acids contains the acrid constituent of the bark, but the authors have not yet been able to isolate this in a condition suitable for investigation (compare Greenish, *loc. cit.*). Hydrolysis, by alkalis, as described below, destroyed this acrid constituent.

The neutral material was hydrolysed by boiling for one hour with potassium hydroxide in alcoholic solution, after which the solution was concentrated, mixed with water, and extracted with ether to remove unsaponifiable matter. This, amounting to 20 per cent. of the original extract, included only a trace of hydrocarbon, or higher aliphatic alcohol, and consisted of semi-solid matter, from which a phytosterol was isolated, which gave a well-marked Liebermann reaction and on acetylation yielded a substance melting at 117°, probably a mixture of acetyl derivatives.

The remaining alkaline liquid was acidified with sulphuric acid, and the mixture distilled in a current of steam, when a yield of about 3·4 per cent. of volatile acids was obtained. The distillate was dissolved in an excess of barium hydroxide solution, the excess of baryta removed by carbon dioxide, and the filtrate concentrated. On adding silver nitrate solution to this liquid, silver was immediately precipitated; moreover, the solution instantly decolorised permanganate, indicating the presence of formic acid. On further concentration a quantity of a sparingly soluble barium salt separated. This was removed and converted into the acid, which was then dissolved in a slight excess of sodium hydroxide, and a silver salt prepared:

0·0413 gave 0·0178 Ag. Ag = 43·1.

$C_8H_{15}O_2Ag$  (silver *n*-octoate) requires Ag = 43·0 per cent.

The aqueous solution of the barium salts from which the above-described acid was separated still contained formic acid, and in

order to remove it, the solution was acidified, shaken with ether, and the ethereal solution well washed with water. In this way a further quantity of acid was obtained, which was fractionally converted into silver salts and the five fractions obtained were analysed:

1. 0.1315 gave 0.0665 Ag. Ag=50.6.
2. 0.1817 „ 0.0934 Ag. Ag=51.4.
3. 0.1448 „ 0.0744 Ag. Ag=51.4.
4. 0.0951 „ 0.0490 Ag. Ag=51.5.
5. 0.0273 „ 0.0141 Ag. Ag=51.7.

$C_5H_9O_2Ag$  (silver valerate) requires Ag=51.6 per cent.

The volatile acids present in the plant appear, therefore, to include formic, valeric, and *n*-octoic acids.

The acid liquid which had been distilled in a current of steam was extracted with ether, and the dark-coloured residue digested twice with petroleum. This left undissolved a dark-coloured, amorphous, resinous substance. The solution when concentrated gave a 23 per cent. yield of fatty acids, which were mixed with the 21 per cent. of free acids (A) previously obtained (see above). The acids were converted into lead salts, which from their behaviour appeared to be a mixture of lead salts of saturated and unsaturated fatty acids.

*Ethereal Extract.*—This consisted of a dark green resin, which on digestion with ether left a quantity of a light coloured substance undissolved. This was almost insoluble in the usual organic solvents except pyridine, from a dilute solution in which it separated in microscopic crystals melting at about  $250^\circ$  and giving the Liebermann reaction, whence it appeared to be a phytosterolin. The ethereal solution was then extracted first with water, removing about 10 per cent. of the extract, and finally with potassium hydroxide solution, which extracted 36 per cent. of acidic resin, leaving neutral resin; none of these yielded any crystalline material.

*Chloroform and Ethyl Acetate Extracts.*—These extracts consisted of amorphous resins. From the chloroform extract there separated gradually a fawn-coloured material, which was not obtained crystalline, nor could a crystalline acetyl derivative be prepared from it.

*Alcoholic Extract.*—This extract was redissolved in alcohol and water added, which precipitated a quantity of a nearly black tar. The clear liquid was treated with an excess of basic lead acetate, the precipitate filtered off, and the lead removed from the precipitate and filtrate by means of hydrogen sulphide in the usual way. The concentrated liquid from the former gave a nearly black colour with

ferric chloride and contained tannin. The concentrated filtrate was evaporated to complete dryness, and finally digested on the water-bath with nine successive portions of about 50 c.c. each of absolute alcohol to separate the large quantity of reducing sugars present. Each fraction was poured from the syrupy residue while hot, and when cold, again poured from a small amount of separated syrup, which was returned to the larger bulk. Crystals separated from each fraction when kept, but only a small quantity from the last. The whole amount of crystalline matter accumulated weighed about 6 grams. This substance proved to be *4-hydroxyhygryic acid*, an optically active acid not previously described.

#### *Examination of the Acid.*

To obtain sufficient material for the identification of the acid, further quantities of the bark were extracted, when the following varying percentage yields were obtained: 0.41, 0.21, and 0.25, amounting in all to 16.35 grams of crude acid.

The product may be readily purified by boiling its solution in water with animal charcoal, repeatedly concentrating the filtrate under diminished pressure with additions of alcohol, until the pure acid separates from the hot solution in colourless needles or prisms, which contain varying amounts of water of crystallisation, thus:

I. 0.1986 lost 0.0170 at 110°.  $H_2O=8.56$ .

II. 0.2108 „ 0.0108 „ 110°.  $H_2O=5.13$ .

Although the acid is very readily soluble in water it may be crystallised from that solvent. 7.05 Grams of substance were dissolved in water, and the solution was concentrated until about 4.5 grams of water remained. The solution was seeded and allowed to remain overnight, when 1.25 grams of the acid had separated in crystals, which appeared to be truncated prisms. These crystals, after being dried in the air, were found to contain one molecule of water:

0.2035 lost 0.0220 at 110°.  $H_2O=10.8$ .

$C_6H_{11}O_3N \cdot H_2O$  requires  $H_2O=11.0$  per cent.

I. 0.1324 \* gave 0.2402  $CO_2$  and 0.0938  $H_2O$ .  $C=49.5$ ;  $H=7.9$ .

II. 0.1090 \* „ 0.1976  $CO_2$  „ 0.0778  $H_2O$ .  $C=49.5$ ;  $H=8.0$ .  
0.1474 gave 12.6 c.c.  $N_2$  at 17° and 746 mm.  $N=9.7$ .

$C_6H_{11}O_3N$  requires  $C=49.6$ ;  $H=7.6$ ;  $N=9.7$  per cent.

*Methoxyl estimation*: 0.1751 gave no AgI.  $MeO=0$ .

*N-Methyl estimation*: 0.1751 „ 0.2430 AgI.  $NMe=17.2$ .

$C_5H_8O_3N \cdot CH_3$  requires  $NMe=20.0$  per cent.

\* Dried at 105°.

The acid decomposes with effervescence at  $242^{\circ}$ , possesses little if any taste, is acid to litmus, but cannot be titrated, is not hygroscopic, and is optically active.

The specific rotatory power was determined in water of (a) a specimen of the acid crystallised from alcohol and containing  $H_2O=5.13$ , and (b) a specimen crystallised from water and containing  $H_2O=10.8$  per cent.:

(a)  $c=4.9910$ ,  $l=1\text{-dm.}$ ,  $\alpha_D - 4.02^{\circ}$ ;  $[\alpha]_D - 80.5^{\circ}$  or  $[\alpha]_D - 84.9^{\circ}$  for the anhydrous substance.

(b)  $c=5.2300$ ,  $l=1\text{-dm.}$ ,  $\alpha_D - 3.98^{\circ}$ ;  $[\alpha]_D - 76.2^{\circ}$  or  $[\alpha]_D - 85.4^{\circ}$  for the anhydrous substance.

It gives a strong pyrrole reaction, and dissolves copper oxide with the formation of a copper salt. A quantity (0.2 gram) of the substance was dissolved in water, and the solution boiled for several hours with an excess of powdered copper oxide, the excess of copper oxide filtered off, and the filtrate concentrated. Blue prisms separated, which were dried on a porous tile, washed with 70 per cent. alcohol, and dried in the air:

0.1021 lost 0.0200 at  $110^{\circ}$ .  $H_2O=19.6$ .

$C_{12}H_{20}O_6N_2Cu, 4H_2O$  requires  $H_2O=17.0$ ;  $C_{12}H_{20}O_6N_2Cu, 5H_2O$  requires  $H_2O=20.4$ .

0.0669 (anhydrous salt) gave 0.0146 CuO.  $Cu=17.4$ .

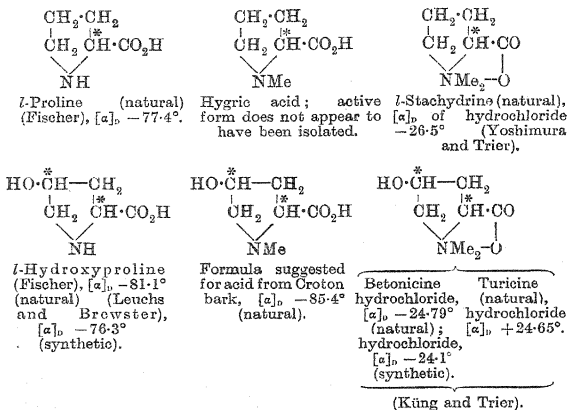
$C_{12}H_{20}O_6N_2Cu$  requires  $Cu=18.1$  per cent.

#### *Constitution of the Acid from Croton gubouga Bark.*

The evidence already given indicates that the substance is a 4-hydroxy-1-methylpyrrolidine-2-carboxylic acid (4-hydroxyhygric acid). Two such compounds have been synthesised by Leuchs and Felsler (*Ber.*, 1908, **41**, 1726), namely, two optically inactive forms of 4-hydroxy-1-methylpyrrolidine-2-carboxylic acid. A comparison of the principal properties of these acids with that from *C. gubouga* bark is given in the following table:

	Formula.	$[\alpha]_D$ .	M. p.	Reaction.	Taste.
Acid from Croton bark .....	$C_6H_{11}O_3N$	$-85.4^{\circ}$	$242^{\circ}$	faintly acid.	little or no taste.
a - 4 - Hydroxy - 1 - methylpyrrolidine-2-carboxylic acid.....	$C_6H_{11}O_3N$	inactive.	$207-208^{\circ}$	neutral.	marked sweet taste
b - 4 - Hydroxy - 1 - methylpyrrolidine-2-carboxylic acid .....	$C_6H_{11}O_3N$	inactive.	$226-227^{\circ}$	faintly acid.	sweetish insipid taste,

Comparison of the specific rotations of the closely related pyrrolidine derivatives indicates that in all probability this acid from Croton bark is 4-hydroxyhygric acid ( $\gamma$ -hydroxy-*N*-methylproline):

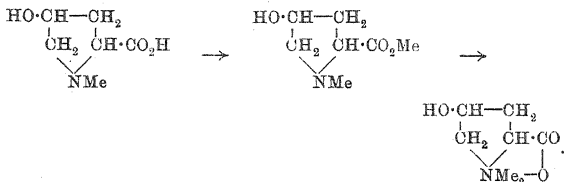


Leuchs and Brewster (*Ber.*, 1913, **46**, 986) have synthesised *l*-hydroxyproline, and Küng (*Zeitsch. physiol. Chem.*, 1913, **85**, 217) on methylating this substance obtained a mixture of the betaines, betonicine and turicine. If, therefore, the acid from *Croton gubouga* bark is in reality 4-hydroxyhygric acid it should in like manner, on methylation, give betonicine and turicine. Küng's method of methylation, with slight modification, was adopted, and resulted in the production of a mixture of betonicine and turicine, thus proving the acid to be 4-hydroxyhygric acid.

Küng (*loc. cit.*) has pointed out that turicine and betonicine are not enantiomorphs. When *l*-hydroxyproline or *l*-hydroxyhygric acid is methylated, using methyl iodide and alkali, it is probable that racemisation occurs and that one of the carbon atoms only, namely, that attached to the carboxyl group, is concerned in the racemisation. It will be interesting to see whether optically active hygric acid, which so far does not appear to have been obtained, and will only possess one asymmetric carbon atom, will yield on methylation two stereoisomeric betaines.

It seemed possible that methylation of the hydroxyhygric acid might be accomplished without racemisation if the use of alkali were avoided, and so evidence might be secured as to which of the

betaines, betonidine or turicine, corresponds with *l*-hydroxyproline and 4-hydroxyhygric acid. It was hoped that by passing hydrogen chloride into boiling methyl alcohol containing 4-hydroxyhygric acid the methyl ester would first be formed, and would pass into the corresponding betaine, thus:



It is probable that the ester was formed, but was rapidly hydrolysed, since on treating the hydrochloride with silver oxide the original 4-hydroxyhygric acid was recovered unchanged.

#### *Methylation of the Acid.*

A preliminary experiment was carried out, using 1 gram of the acid, which was dissolved in a mixture of 2 c.c. of water and 20 c.c. of methyl alcohol. Five c.c. of a solution of 6 grams of potassium hydroxide in 100 c.c. of methyl alcohol, and a like quantity of a solution of methyl iodide in methyl alcohol (3 grams in 20 c.c.), were added alternately 1 c.c. at a time. As the solution remained alkaline, a further 5 c.c. of the methyl iodide solution were added, and the mixture boiled on a water-bath for half an hour. One c.c. of methyl iodide was then added and sufficient methyl-alcoholic potassium hydroxide to render the liquid alkaline. The solution was boiled for about twenty minutes and made alkaline, again boiled for five minutes and made alkaline, and the operation repeated until the alkalinity persisted. The alcohol was distilled off, the residue dissolved in water, the solution made slightly acid with hydrochloric acid, and boiled with excess of silver chloride. The silver iodide and excess of silver chloride were filtered off, and the filtrate evaporated to dryness under diminished pressure. The residue was treated with absolute alcohol and again evaporated to dryness. The dry residue was extracted with five small quantities of boiling absolute alcohol; the first three of which removed all but traces of the hydrochlorides of the betaines. The alcohol was distilled off and the rotation of the residue determined, using water as solvent ( $c=6.4275$ ,  $l=1\text{-dm.}$ ,  $\alpha_D +0.075^\circ$ ;  $[\alpha]_D +1.2^\circ$ ).

This result indicated that the methylation had proceeded as expected, and that a mixture of turicine and betonicine hydrochlorides in about equal amounts had been produced.

Küng and Trier (*loc. cit.*) pointed out the difficulty of separating turicine and betonicine by fractional crystallisation of their hydrochlorides, and recommended for this purpose the free bases. This the authors are able to confirm, since on dissolving the mixed hydrochlorides having  $[\alpha]_D + 1.2^\circ$  in absolute alcohol, concentrating and allowing to crystallise, 0.667 gram of a mixture of rosettes of needles, and rosettes of plates was obtained which gave  $[\alpha]_D + 3^\circ$  ( $c=3.335$ ,  $l=1$ -dcm.,  $\alpha_D + 0.10^\circ$ ), and on further recrystallisation a mixture of crystals amounting to 0.456 gram and having  $[\alpha]_D + 5.0^\circ$  ( $c=2.280$ ,  $l=1$ -dcm.,  $\alpha_D 0.115^\circ$ ) was obtained. The various solutions were united, the alcohol was removed by distillation under diminished pressure, and the free bases were liberated by treating the aqueous solution with excess of silver oxide. The silver chloride and excess of silver oxide were filtered off, the filtrate was concentrated, absolute alcohol added, and the solution again concentrated, this operation being repeated until crystals separated out on cooling. 0.137 Gram of substance crystallised in long prisms, which had a sweet taste, decomposed at  $250^\circ$  with frothing, and gave  $[\alpha]_D + 21.2^\circ$  ( $c=2.6400$ ,  $l=1$ -dcm.,  $\alpha_D + 0.58^\circ$ ).

Five grams of the acid were then methylated as described above with slight modifications. The same proportions of methyl iodide, methyl-alcoholic potassium hydroxide and acid were used, but the solutions were more concentrated. The alcoholic solution of the mixed hydrochlorides from the extraction of the dried mixture of potassium chloride and betaine hydrochlorides was kept overnight to separate as much potassium chloride as possible. When the hydrochlorides had been converted into bases by treating their aqueous solution with silver oxide and the silver chloride and undissolved excess of silver oxide removed by filtration, hydrogen sulphide was passed through the solution of the bases to remove any silver in solution. The solution of the betaines was concentrated to low bulk under diminished pressure, alcohol added, and the solution again concentrated; this operation was repeated until crystallisation set in on cooling. From the mother liquor two further crops were obtained on concentration.

*Crop I* consisted of nearly pure turicine, amounting to 1.7 grams. The air-dried substance was examined polarimetrically in water:

$$c=2.5330, l=1\text{-dcm.}, \alpha_D + 0.87^\circ; [\alpha]_D + 34.3^\circ.$$

On recrystallisation until the optical rotation was constant, the value  $[\alpha]_D + 40.9^\circ$  was obtained for the anhydrous substance.

*Crop II* weighed 1.2 grams and was a mixture:

$$c = 2.5840, l = 1\text{-dcm.}, \alpha_D - 0.48^\circ; [\alpha]_D - 18.6^\circ.$$

*Crop III*, weighing 1.06 grams, was also a mixture:

$$c = 2.6180, l = 1\text{-dcm.}, \alpha_D - 0.41^\circ; [\alpha]_D - 15.7^\circ.$$

Crops II and III were united, converted into hydrochlorides, dissolved in absolute alcohol, and the solution was concentrated, when 1.45 grams of nearly pure betonicine hydrochloride crystallised out:

$$c = 3.3765, l = 1\text{-dcm.}, \alpha_D - 0.75^\circ; [\alpha]_D - 22.2^\circ.$$

As it was found difficult to remove all traces of potassium chloride from the betonicine hydrochloride, and it was not possible to obtain a higher value than  $[\alpha]_D - 22.9^\circ$  on recrystallising this particular specimen, a further methylation of the acid was tried with good results, using sodium hydroxide instead of potassium hydroxide; with this difference, 3.9 grams of the acid were methylated as in the previous experiment; 1.2731 grams of crude turicine were obtained as a first crop:

$$c = 6.3655, l = 1\text{-dcm.}, \alpha_D + 2.25^\circ; [\alpha]_D + 35.3^\circ \text{ for the anhydrous substance.}$$

The bases in the mother liquor were converted into hydrochlorides, and crystallised from absolute alcohol; 1.322 grams of nearly pure betonicine hydrochloride were obtained, having  $[\alpha]_D - 22.7^\circ$  ( $c = 6.6100, l = 1\text{-dcm.}, \alpha_D - 1.50^\circ$ ). This was recrystallised until its optical rotation remained constant, the highest reading being  $[\alpha]_D - 24.8^\circ$  ( $c = 3.5900, l = 1\text{-dcm.}, \alpha_D - 0.89^\circ$ ).

The bases in the mother liquor from the betonicine hydrochloride ( $[\alpha]_D - 22.7^\circ$ ) were regenerated by treatment with silver oxide. On crystallisation from alcohol a further 0.4012 gram having  $[\alpha]_D + 4.0^\circ$  ( $c = 2.0060, l = 1\text{-dcm.}, \alpha_D + 0.08^\circ$ ) was obtained.

The formation of a mixture of turicine and betonicine by the methylation of the acid from *Croton gubouga* bark leaves no doubt that the acid is 4-hydroxyhygric acid, as formulated on p. 928.

#### *Properties of Turicine.*

Turicine crystallises from alcohol in flat prisms containing one molecule of water of crystallisation, which it rapidly loses in a vacuum desiccator. It is neutral to litmus, is not hygroscopic, has a sweet taste, and gives an intense pyrrole reaction. The anhydrous substance decomposes with frothing at  $260^\circ$ , as did a specimen kindly supplied by Prof. A. K $\ddot{u}$ ng; the decomposition point was not depressed on mixing the two specimens. The hydrated substance commenced to melt at about  $249^\circ$ , but finally decomposed with frothing at  $256^\circ$ . Prof. K $\ddot{u}$ ng's specimen, and a mixture of the



two, behaved in the same way. (Found,  $\text{H}_2\text{O}=10.59$ ;  $\text{C}_7\text{H}_{13}\text{O}_3\text{N}, \text{H}_2\text{O}$  requires  $\text{H}_2\text{O}=10.17$ . Found,  $\text{C}=52.7$ ;  $\text{H}=8.3$ .  $\text{C}_7\text{H}_{13}\text{O}_3\text{N}$  requires  $\text{C}=52.8$ ;  $\text{H}=8.2$  per cent.)

The specific rotations of three specimens of the anhydrous substance were determined in water:

- I.  $c=1.8065$ ,  $l=1\text{-dcm.}$ ,  $\alpha_D + 0.75^\circ$ ;  $[\alpha]_D + 41.5^\circ$ .
- II.  $c=1.3950$ ,  $l=1\text{-dcm.}$ ,  $\alpha_D + 0.57^\circ$ ;  $[\alpha]_D + 40.9^\circ$ .
- III.  $c=2.0980$ ,  $l=1\text{-dcm.}$ ,  $\alpha_D + 0.85^\circ$ ;  $[\alpha]_D + 40.5^\circ$ .

Küng and Trier give  $[\alpha]_D + 36.26^\circ$  for the hydrated betaine corresponding with  $[\alpha]_D + 40.4^\circ$  for the anhydrous substance.

*Turicine Hydrochloride.*—This was prepared from the pure base. When crystallised rapidly from absolute alcohol it separated in needles, but when allowed to crystallise slowly, six-sided tablets were obtained. It is acid to litmus, and decomposes with frothing at  $224^\circ$ ; Küng and Trier give  $222^\circ$  and  $223^\circ$  as the melting and decomposing point. Its specific rotation was determined in water.  $c=2.8000$ ,  $l=1\text{-dcm.}$ ,  $\alpha_D + 0.72^\circ$ ;  $[\alpha]_D + 25.7^\circ$ . Küng and Trier give  $[\alpha]_D + 24.65^\circ$ , and state that turicine is not hygroscopic, but the authors are of the opinion that it is slightly hygroscopic.

Turicine aurichloride was obtained by adding gold chloride solution to a concentrated aqueous solution of turicine hydrochloride. The crystals, which separated rapidly, were collected, dissolved in hot water, and the solution was allowed to cool, when the double chloride crystallised in clusters of yellow prisms. The decomposition point was determined in the same bath with a specimen of turicine aurichloride kindly supplied by Prof. Küng, and a mixture of the two specimens; the decomposition with frothing occurred in each case at  $230\text{--}232^\circ$ . Küng and Trier give the melting and decomposing point as  $232^\circ$ . (Found,  $\text{Au}=39.0$ ;  $\text{C}_7\text{H}_{13}\text{O}_3\text{N}, \text{HAuCl}_4$  requires  $\text{Au}=39.5$  per cent.)

#### *Properties of Betonicine.*

The free base was obtained from the pure hydrochloride by treating with silver oxide. It crystallises anhydrous from alcohol in short, four-sided, truncated pyramids, is more readily soluble in alcohol than turicine, has a sweet taste, is neutral to litmus, and gives an intense pyrrole reaction. Küng and Trier state that it is not hygroscopic, and that it melts and decomposes at  $243\text{--}244^\circ$ ; the purest specimen obtained by the authors was slightly hygroscopic and decomposed with frothing at  $252^\circ$ . (Found,  $\text{C}=52.7$ ;  $\text{H}=8.5$ .  $\text{C}_7\text{H}_{13}\text{O}_3\text{N}$  requires  $\text{C}=52.8$ ;  $\text{H}=8.2$  per cent.) The specific rotation was determined in water:

$$c=3.5050, l=1\text{-dcm.}, \alpha_D - 1.23^\circ; [\alpha]_D - 35.1^\circ.$$

Küng and Trier give  $[\alpha]_D -36.6^\circ$ .

Betonicine hydrochloride crystallises from absolute alcohol in needles or prisms, which, after drying at  $105^\circ$ , decompose with frothing at  $227^\circ$ ; a specimen supplied by Prof. Küng, which was slightly coloured, after drying at  $105^\circ$ , decomposed with frothing at  $224^\circ$ ; a mixture of the two specimens decomposed at an intermediate temperature. Küng and Trier give the melting and decomposing point as  $222-223^\circ$ . The hydrochloride is not hygroscopic and is acid in reaction. The specific rotatory power was determined in water:

$$c=3.5900, l=1\text{-dm.}, \alpha_D-0.89^\circ; [\alpha]_D-24.8^\circ.$$

Küng and Trier give  $[\alpha]_D-24.79^\circ$  for natural betonicine hydrochloride, and Küng  $[\alpha]_D-24.1^\circ$  for his synthetic product.

*Betonicine Aurichloride.*—To a concentrated solution of betonicine hydrochloride a solution of gold chloride was added. There was no immediate separation of crystals as in the case of turicine hydrochloride. The solution was accordingly concentrated and, on cooling, four-sided, yellow plates crystallised out. When redissolved in hot water and kept, clusters of yellow tablets were obtained. The substance decomposed with frothing at  $230-232^\circ$ , the same temperature as a specimen supplied by Prof. Küng, and a mixture of the two specimens also decomposed at this point. (Found,  $\text{Au}=39.2$ .  $\text{C}_7\text{H}_{13}\text{O}_3\text{N}, \text{HAuCl}_4$  requires  $\text{Au}=39.5$  per cent.)

The authors desire to take this opportunity of thanking Prof. Küng for his kindness in supplying them with specimens of turicine, turicine aurichloride, betonicine hydrochloride, and betonicine aurichloride for comparison.

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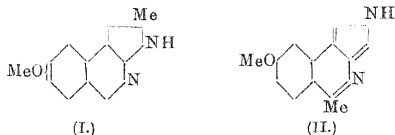
[Received, July 9th, 1919.]

## LXXIX.—*Harmine and Harmaline. Part III.*

By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

IN 1912 the present authors, having located in the harmine molecule a methyl group similarly situated to that in quinaldine, suggested that the alkaloid contains a fused ring system comprising a benzene, pyrrole, and pyridine nucleus, and constructed a constitutional formula (T., 101, 1775) which satisfied the requirements of the facts then known. This expression (I) was discarded by O. Fischer (*Ber.*, 1914, 47, 99) in favour of the formula II on account of his

discovery that harminic acid\* may be oxidised by nitric acid in a sealed tube with the formation of *isonicotinic acid* (III), and this observation was held to be inconsistent with the assumption made in I that there is an imino-group attached to the pyridine ring :

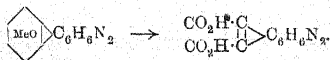


As the result of a further examination of derivatives of harmine and harmaline we are now convinced that neither of these formulae is correct, and, after a careful reconsideration of the whole subject, have deduced fresh expressions which it is believed are more satisfactory representations of the chemistry of these bases. The argument which has been developed may be presented in the following sections.

#### *The Ring System of Harmine and its Derivatives.*

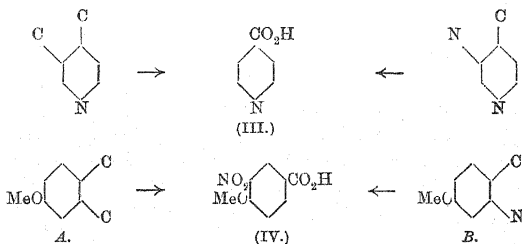
Harmine,  $C_{13}H_{12}ON_2$ , contains a methyl and a methoxyl group and may be written  $C_{11}H_6N_2Me \cdot OMe$ , and is therefore a derivative of a substance,  $C_{11}H_8N_2$ . Although the methoxyl and methyl groups have been separately eliminated with the production of compounds called harman and norharmine respectively, the parent,  $C_{11}H_8N_2$ , which might be called *norharman*, has not yet been prepared. Now harmaline, which is dihydroharmine, yields *m*-nitroanisic acid (IV) on oxidation with nitric acid (O. Fischer and Boesler, *Ber.*, 1912, **45**, 1934), whilst the production of *isonicotinic acid* has already been referred to above. The existence of both benzene and pyridine nuclei in norharman is therefore certain, and, on inspection of the composition, it will be seen that there is no alternative to the theory that this substance must contain a benzene, pyridine, and pyrrole nucleus fused together as are the benzene nuclei in anthracene or phenanthrene. So much was already recognised, and in addition that the benzene nucleus occupies a terminal position in the system, a fact which follows from the consideration of the relation of harminic acid to harmine. It is neces-

\* This acid is obtained from harmine by oxidation with chromic acid (O. Fischer and E. Tauber, *Ber.*, 1885, **18**, 403).



sary to recall these points in order to develop the present discussion.

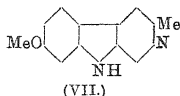
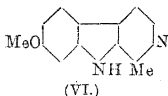
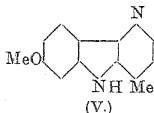
When a compound containing a fused ring system is energetically oxidised, it is usual to be able to recognise, in the product, residual groups which are derived from the nucleus destroyed by the oxidation and are situated at both the points of fusion of the original rings. Yet, in the degradation of harmine, this rule is not followed in the two cases which have been already mentioned, namely, the production of nitroanisic acid from harmaline (or nitroharmaline) and that of *isonicotinic acid* from harminic acid. In both these reactions one of the positions of ring fusion is represented by a hydrogen atom in the oxidation product. It will be necessary to assume the possibilities shown under *A* or *B* below, and these are clearly the only alternatives:



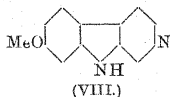
In attempting to make a choice from these alternatives, neither of which is quite in accord with previous experience, we have been guided by two main considerations. The first is that the conditions of elimination of carbon from direct union with aromatic nuclei are much better understood than those governing the similar removal of nitrogen, and whereas experimental and other evidence is not at present available to enable us to refute the alternative *B*, we are on much firmer ground in regard to *A*, which we consider is opposed to experience. O. Fischer suggested that a nitromethoxyphthalic acid is the intermediate product in the oxidation of harmaline, and that this loses carbon dioxide with the formation of nitroanisic acid. The supposed intermediate product does not, however, appear to have been isolated, and we can find no record in the literature of an analogous reaction in which a phthalic acid at all similarly constituted loses one of its carboxyl groups under comparable conditions. In the production of *isonicotinic acid* scheme *A* makes it necessary to assume the elimination of carbon

attached to the  $\beta$ -position in a pyridine nucleus, whilst that in the  $\gamma$ -position remains in the form of a carboxyl group. When it is remembered that, of the three pyridinemonomonocarboxylic acids, it is only nicotinic acid which requires to be heated with soda-lime in order to convert it into pyridine, and, further, that quinolinic acid and cinchomeronic acid both yield nicotinic acid on being strongly heated, it will be realised how relatively firm is the attachment of carbon to the  $\beta$ -position. It is consequently very improbable from this point of view that a pyridine derivative convertible into isonicotinic acid by a simple oxidation process can have a carbon atom attached to the  $\beta$ -position. The second argument in favour of the assumption that these degradations involve the elimination of nitrogen, and not of carbon, from direct combination with the surviving nuclei, is that we have obtained experimental indications that the benzene nucleus of a harmine derivative is actually directly attached to a nitrogen atom. Tetrahydroharmine,  $C_{13}H_{16}ON_2$ , condenses with diazobenzenesulphonic acid with the formation of a sparingly soluble, crystalline, orange-yellow azo-compound,  $C_{13}H_{15}ON_2 \cdot N_2 \cdot C_6H_4 \cdot SO_3H$ , which dyes silk yellow from an acid bath, behaves as an indicator, and undergoes changes with acid and alkali closely resembling those characteristic of methyl-orange. Comparison with a large number of azo-derivatives of various types derived from diazobenzenesulphonic acid and such second components as dihydroberberine, anhydrocryptopine,  $\beta$ -dialkylamino-crotonic esters,  $\beta$ -diketones, pyrrole,  $\alpha$ - and  $\beta$ -methylindole and indole, showed that the change from yellow to crimson is exhibited only by the true benzeneazobenzene derivatives. It would therefore appear that tetrahydroharmine is an aniline derivative with a free para-position, and naturally the argument applies to all the bases of the group so far as it throws light on their nuclear structure. We are therefore compelled to accept this surprising elimination in a nitric acid oxidation of a side-chain commencing with a nitrogen atom, and in attempting to form an idea as to the possible mechanism of the reaction the clue seems to be given by the oxidation of phenylhydrazine with the production of benzene. Possibly, the imino-group of harmine becomes converted into the nitroamino- or nitrosoamino-group, and one of these becomes reduced by readily oxidisable groups produced in the course of the reaction, so that, at a certain stage, the condition is reached at which nitrogen is eliminated and hydrogen replaces the whole side-chain. Accepting scheme *B* and its implications, it is quite clear that if harmine contains no carbon attached to its pyridine nucleus in the  $\beta$ -position, this nucleus cannot be fused with a benzene ring and harmine cannot be a derivative of quinoline or isoquinoline. The order of

fusion of rings is, then, benzene-pyrrole-pyridine, and the methyl group must be in the pyridine nucleus. Further, the only possible formulæ for harmine, bearing in mind the formation of nitroanisic acid from harmaline, are the following:



In V the methyl group is in the  $\gamma$ -position in the pyridine ring, and this is inconsistent with the behaviour of harmine, which, as we have already stated, closely resembles quinaldine in its reactions. It shows the quinophthalone reaction and condenses with benzaldehyde to benzylideneharmine, a styryl derivative, which may be oxidised to norharminecarboxylic acid (T., 1912, 101, 1784). The latter gives a red coloration with ferrous sulphate, and easily loses carbon dioxide, on heating in glycerol, with the formation of norharmine. We therefore reject the structure V, and consider harmine must be either VI or VII, and since these differ only in the position attributed to the methyl group, the constitution of norharmine is determined and is shown in VIII:



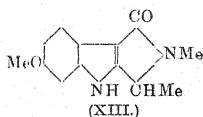
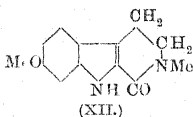
### *The Constitution of Harmine.*

The decision between formulæ VI and VII for harmine is a difficult one, and cannot at present be made with precision, but there are strong indications which cause us to much prefer the former alternative. A glance at the structure of norharmine will show that it is a species of *isoquinoline* in which indole takes the place of benzene. Alkaloids of the *isoquinoline* group are known which contain a methyl group in their pyridine or reduced pyridine rings, and of these corydaline has been most completely investigated. The methyl group in VI is in the position which an analogy to corydaline would suggest. Further light is thrown on the problem by the study of the oxidation of *N*-methyltetrahydroharmine, and some preliminary remarks must be made in regard to the constitution of this substance. Harmine or harmaline, by reduction in acid or alkaline solution, yields the same tetrahydroharmine as the end-

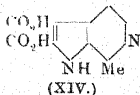


A curious analogy between tetrahydroharmine and 2:3-dimethylindole is shown by the colour reactions with *p*-dimethylaminobenzaldehyde and aqueous-alcoholic hydrochloric acid on heating. The dimethylindole slowly develops a pale blue colour, which fades to pale greenish-yellow on cooling the solution, and the alternation of colours on heating and cooling can be made as often as desired. Tetrahydroharmine behaves entirely similarly except that the hot liquid is bluish-pink and the cold solution yellow.

Returning to the question of the position of the methyl group in harmine, *N*-methyltetrahydroharmine will be X or XI according as harmine is taken as VI or VII respectively. On oxidation with potassium permanganate in acetone solution this base,  $C_{14}H_{18}ON_2$ , is partly converted into a neutral substance melting at  $228^\circ$ , which has the composition  $C_{13}H_{14}O_2N_2$ , and clearly the newly acquired oxygen atom forms part of a carbonyl group which by direct union with the basic nitrogen neutralises its salt-forming character. At the same time the oxidation has removed a carbon atom, most probably originally in the form of a methyl group. This substance (m. p.  $228^\circ$ ) was recovered unchanged after heating at  $100^\circ$  with phosphorus pentachloride and phosphoryl chloride, although a clear solution was obtained. On the basis of formula XI for *N*-methyltetrahydroharmine, all possible structures for the oxidation product will contain either the grouping  $\cdot NH \cdot CO \cdot$  or  $\cdot CH_2 \cdot CO \cdot$ , and in either case a reaction with phosphorus pentachloride would be anticipated. Assuming formula X, however, it is possible to construct two expressions (XII and XIII) for the compound (m. p.  $228^\circ$ ), which are in harmony with its composition and other properties:



The evidence, just mentioned, is not quite conclusive, since the apparent failure to react with phosphorus pentachloride may have been due to the ready hydrolysis of the chloro-derivative by water, but, so far as it goes, it favours formula VI for harmine, and we have therefore provisionally adopted this expression. It follows that harminic acid and *apoharmine* must be represented by XIV

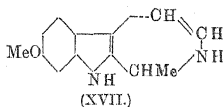
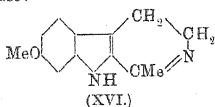




and XV respectively, and since harminic acid is no longer to be regarded as a pyridine- $\alpha\beta$ -dicarboxylic acid, the elimination on heating of both carboxyl groups becomes explicable.

### *The Constitution of Harmaline.*

Since harmaline may be oxidised to harmine (Fritzsche, *Annalen*, 1848, **64**, 365; O. Fischer, *Ber.*, 1889, **22**, 640) and reduced to tetrahydroharmine, it is to be regarded as dihydroharmine, and the most probable constitutional formulæ for the base are shown in XVI and XVII. The available evidence does not all point in one direction, but, on the balance, we favour the structure XVI as being the better summary of the relations and properties of the base:



In support of the expression XVI the following considerations may be noted *inter alia*.

(1) The harmaline metho-salts, for example, the metho-chloride (see p. 952), are quaternary salts and give no precipitate on the addition of ammonia to their aqueous solutions.

(2) The fact that harmaline occurs in the seeds of *Peganum harmala* in an optically inactive condition is consistent with a formula like XVI, which contains no asymmetric carbon atom, whilst, on the other hand, a base having the constitution XVII, which implies the possibility of the existence of enantiomorphic modifications, would most probably occur in a plant in an optically active condition.

(3) Harmaline shows a tendency to form additive products, for example, with hydroxylamine (O. Fischer, *Ber.*, 1914, **47**, 105) and with hydrogen cyanide (Fritzsche, *Annalen*, 1848, **68**, 351; 1849, **72**, 307). The product of the latter process, cyanodihydroharmaline, is a base, and the whole reaction is reminiscent of that between cotarninium or hydrastinium salts and potassium cyanide. Like cyanohydrocotarnine, cyanodihydroharmaline is resolved into its components on warming with a mineral acid. The ketimino-type structure of XVI furnishes an explanation of these additive reactions.

(4) The oxidation of tetrahydroharmine with production of harmaline (see below) is more readily understood with the aid of the formula XVI than with XVII.

The more important arguments in favour of XVII are the following:

(1) Harmaline forms an acetyl derivative and an *N*-methyl derivative closely resembling the parent base.

(2) Harmaline condenses with diazonium salts with formation of bisazo-compounds (O. Fischer and W. Boesler, *Ber.*, 1912, 45, 1930). On the assumption that XVII is correct, this behaviour is explicable since one point of coupling would be in the benzene ring as in the case of tetrahydroharmine, whilst the second point of attack is in the group  $\cdot\text{CH}:\text{CH}\cdot\text{NH}\cdot$ , which is contained as such or in a homologous form in many non-benzenoid substances which form azo-derivatives on treatment with diazonium salts.

(3) The possibility of migration of the ethylene linking may be held to discount to some extent the arguments 1 and 2 advanced in support of formula XVI.

A formula for harmaline must be grounded on a knowledge of the constitution of harmine, and until the position of the methyl group in the latter is known with a greater approach to certainty it is impossible to be quite sure that there is no alternative to the suggestions which have been discussed.

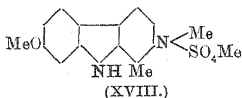
Harmaline forms a normal methosulphate which is readily oxidised by potassium permanganate in acetone solution (see p. 960), yielding the substance (m. p.  $228^{\circ}$ ) mentioned above as the oxidation product of *N*-methyltetrahydroharmine. There is therefore an interdependence between the constitutions assumed for harmaline and for the substance melting at  $228^{\circ}$ . Formula XVI for harmaline corresponds with XII for the oxidation product, whilst XIII for this substance and XVII for harmaline are similarly related.

### *Methylharmine.*

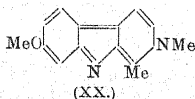
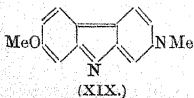
It has been tacitly assumed that the basic nitrogen of harmine is that which is contained in the pyridine nucleus, and the basis of this theory may now be more particularly stated. Harmine closely resembles carbazole in constitution, and the nitrogen atom of carbazole is almost devoid of basic character, so that the similarly situated nitrogen of the imino-group of harmine should also lack salt-forming character. This point of view is supported by the fact that harmine is similar to carbazole in the degree of reactivity of its benzene nucleus and by the correspondence in properties between tetrahydroharmine and a dialkylindole. Again, the metho-salts of harmine are quaternary salts, so that they can scarcely have been formed by addition to an imino-group, and these salts exhibit the

same fluorescence in aqueous solution as a harmine salt. Finally, *N*-acetyltetrahydroharmine is not a base.

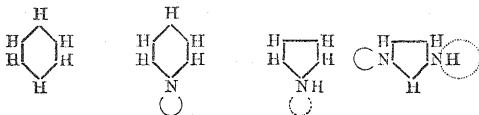
Accordingly, if harmine is VI, harmine methosulphate (p. 951), which is typical of the harmine metho-salts, must be represented by the formula XVIII:



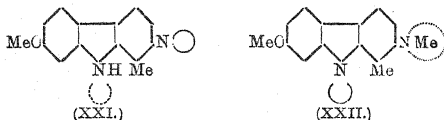
An aqueous solution of this salt gives no precipitate with ammonia or even with very dilute sodium hydroxide, but, on the addition of more sodium hydroxide, a yellow, chalky precipitate is obtained, and this appears to have the composition  $C_{14}H_{14}ON_2 \cdot 3H_2O$ , and is probably the quaternary ammonium hydroxide corresponding with XVIII with two molecules of water of crystallisation. By heating at  $100^\circ$  this hydrated material is changed into methylharmine melting at  $209^\circ$  (compare O. Fischer, *Ber.*, 1897, **30**, 2482). The salts of this substance with acids are identical with the corresponding metho-salts of harmine, and it is reconverted into the ammonium hydroxide by boiling with water. There are three possible ways of representing the elimination of water from harmine methohydroxide with the formation of methyl harmine. In the first place a group,  $:N:CH_2$ , might be formed, but this would result in an unusual type of quinquivalent nitrogen, and if this were the true explanation the loss of water from methylpyridinium hydroxides and methylquinolinium hydroxides with the formation of methylpyridines and methylquinolines might be anticipated. The second view might be that the C-methyl group is involved,  $\cdot C(CH_3):NMe(OH) \cdot$ , being changed into  $\cdot C(:CH_2) \cdot NMe \cdot$ . This possibility is excluded by the observation (p. 951) that norharmine methosulphate on decomposition with hot aqueous sodium hydroxide yields a methylnorharmine entirely resembling methylharmine. The third and only remaining alternative quite free from objection is that water is eliminated by the combination of the hydroxyl of the quaternary ammonium hydroxide and the hydrogen of the imino-group in the pyrrole nucleus. This leads to the formulæ XIX and XX for methylnorharmine and methylharmine respectively:



These formulæ are based on a conception of the nature of aromatic types which is comparable to that expressed in the Kekulé benzene formula, and it is on this account that the arrangement of the valencies appears somewhat unusual and the close relation with harmine is obscured. If, however, the symbols



are employed for benzene, pyridine, pyrrole, and glyoxaline respectively, the corresponding expressions for harmine and methylharmine are XXI and XXII, and it will be seen that the difference between the ring-systems is almost confined to the function of the nitrogen atoms. The thickened lines in all these formulæ represent a sesqui-valency and the dotted loops attached to the nitrogen atoms indicate that a partial use for nuclear conjugation has been made of the latent valencies.



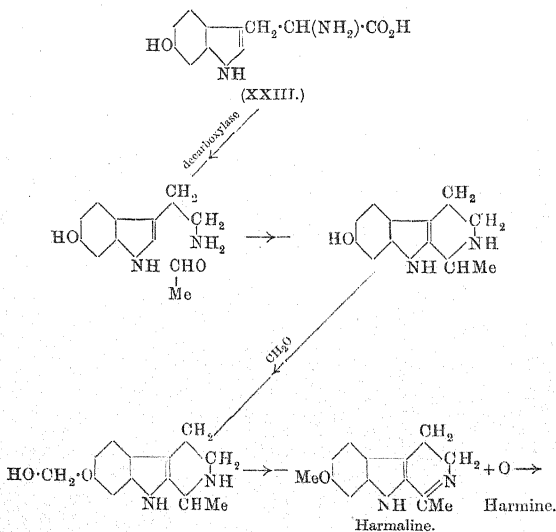
On gently warming with sulphuric acid, methylharmine is sulphonated and an extremely sparingly soluble, colourless substance,  $C_{14}H_{14}O_4N_2S$ , is precipitated on the addition of water. In view of the fact that methylharmine may be regenerated by prolonged boiling with dilute hydrochloric acid, this compound may be the anhydride of harmine methohydroxide *N*-sulphonic acid. A similar pale yellow, sparingly soluble substance,  $C_{14}H_{16}O_4N_2S$ , is obtained by warming harmaline methochloride with concentrated sulphuric acid and pouring the solution into water. The sulphonic group may also be in the benzene nucleus, and the matter is being further investigated.

#### *The Synthesis of Harmine and Harmaline in the Plant.*

One of the strongest arguments in favour of the main outlines of the views which have been developed above is that, unlike the older formulæ, the new expressions contain a ring-system which is related to that of an important and widely distributed amino-acid, namely, tryptophan. The actual starting point is, however, not

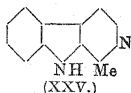
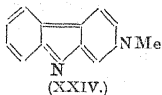
tryptophan itself, but a hydroxytryptophan bearing the relation to the former substance which tyrosine bears to phenylalanine. We venture to predict that this hydroxytryptophan (XXIII) will be found among the amino-acids derived from vegetable proteins.

Abderhalden and Baumann (*Zeitsch. physiol. Chem.*, 1908, 55, 412) have, indeed, already stated that tryptophan is generally found in combination with a hydroxytryptophan, but it does not appear that a description of this substance has been published, and there is no evidence that the hydroxyl group is in the benzene ring. The elaboration of hydroxytryptophan (XXIII) into harmine is shown in the following scheme, and is strictly parallel with the phytochemical synthesis of an *isoquinoline* alkaloid :



The acetaldehyde required probably arises from the oxidation of alanine. This scheme implies the production of the tetrahydroharmine ring in the first place, and this later becomes oxidised to harmaline and harmine. In this connexion experimental evidence is not lacking since we have found (p. 961) that tetrahydroharmine may be oxidised to harmaline by means of potassium permanganate.

in acetone solution and the further oxidation of harmaline to harmine has also been effected (*loc. cit.*). Thus by oxidation of tetrahydroharmine the intermediate stage can be realised, whilst harmaline has never been detected as one of the products of reduction of harmine. Indeed, the conversion of harmine into harmaline by any process has never previously been possible and has only become practicable through the intermediary of tetrahydroharmine, which is obtainable from harmine. The crystalline base,  $C_{12}H_{10}N_2$ , which Hopkins and Cole (*J. Physiol.*, 1902, **29**, 451) obtained from tryptophan by oxidation with ferric chloride may possibly owe its formation to a reaction similar to that assumed above in the vital synthesis of harmine. It is clear that the carboxyl group of tryptophan has been eliminated, and therefore  $C_2$  has been added, and this may be due to the presence of formaldehyde (2 mols.) or of some oxygenated ethane derivative or the equivalents of these derived from a degradation of a second molecule of tryptophan. The two most probable formulæ are XXIV and XXV, and, since the base melts at  $238^\circ$ , perhaps the latter is preferable, as this melting point would be rather high for an *N*-methyl derivative of this type. Thus harmine melts at  $257^\circ$  and methylharmine at  $209^\circ$ ; harmaline melts at  $238^\circ$  and methylharmaline at  $162^\circ$ ; apoharmine melts at  $183^\circ$  and methylapoharmine at  $78^\circ$ :

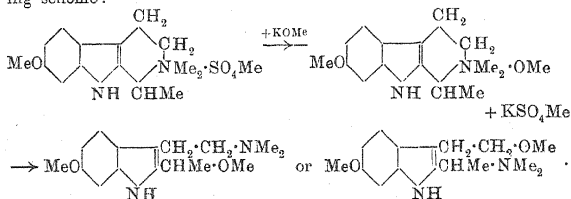


Formula XXV is, however, the constitution on the basis of our views of harmine which melts at  $230^\circ$  (O. Fischer, *Chem. Centr.*, 1901, i, 957), and in spite of this difference in melting point we consider there is a possibility that the two substances may be identical.

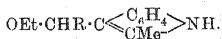
#### *A Ring-fission of a Harmine Derivative.*

Up to the present the harmine ring has resisted all attempts to open it without loss of carbon or nitrogen, and on this account especial interest attaches to the investigation of a colourless base (m. p.  $129^\circ$ ), which O. Fischer first prepared by the decomposition of methyltetrahydroharmine methiodide by means of methylalcoholic potassium hydroxide (*Ber.*, 1914, **47**, 104). We have obtained the same substance from the normal methosulphate of methyltetrahydroharmine, by boiling with methylalcoholic potassium hydroxide, but find its composition to be  $C_{16}H_{24}O_2N_2$ , instead of  $C_{15}H_{22}O_2N_2$ , as suggested by Fischer. A Zeisel estimation

showed the presence of two methoxyl groups, so that the additional carbon atom is most probably derived from the methyl alcohol used as solvent, and this was confirmed by the fact that when ethyl-alcoholic potassium hydroxide was employed in the reaction a new substance,  $C_{17}H_{26}O_2N_2$ , was obtained. Unfortunately, the latter compound could not be crystallised, but the analytical results were sufficiently satisfactory to establish the point at issue. The base (m. p.  $129^\circ$ ) is produced in our view in accordance with the following scheme:



The fact that ethers of this kind are readily formed has been demonstrated by M. Scholtz (*Ber.*, 1913, **46**, 2138), who found that aldehydes react with 2-methylindole in alcoholic solution in the presence of sodium hydroxide with the formation of substances of the type



#### EXPERIMENTAL.

##### *Harmine Metho-salts.*

*Harmine Methosulphate*,  $C_{13}H_{12}ON_2 \cdot \text{Me}_2\text{SO}_4$ .—This derivative is readily prepared by rubbing harmine (1 gram) into a paste with methyl sulphate (1 c.c.), leaving for twenty-four hours, and then dissolving the solid product in boiling methyl alcohol. On cooling, the methosulphate separates as a pale yellowish-green, crystalline mass, and, after repeated recrystallisation, is obtained almost colourless. In preparing larger quantities, a good plan is to cover the finely powdered harmine with benzene, and, after adding the methyl sulphate, to heat on the steam-bath, when combination takes place rapidly and is complete in half an hour. The product is washed with benzene by the aid of the pump and drained on porous porcelain. A specimen, which had been crystallised from water and left exposed to the air until dry, yielded the following analytical results:

0.1288 lost 0.112 at 100°.  $H_2O = 8.7$ .

\*0.1176 gave 0.2316  $CO_2$  and 0.0580  $H_2O$ .  $C = 53.7$ ;  $H = 5.3$ .

$C_{13}H_{12}ON_2 \cdot Me_2SO_4 \cdot 2H_2O$  contains  $H_2O = 9.6$  per cent. and

$C_{13}H_{12}ON_2 \cdot Me_2SO_4$  requires  $C = 53.3$ ;  $H = 5.3$  per cent.

*Harmin methosulphate* melts at about 220° and is readily soluble in hot water, from which it separates as a voluminous mass of needles; it is also readily soluble in boiling methyl alcohol, but much less so in the cold. The aqueous solution is not precipitated by ammonia, but sodium hydroxide gives at once a voluminous, yellow, crystalline precipitate of the hydrated ammonium hydroxide (see p. 948).

*Harmin Methiodide*,  $C_{13}H_{12}ON_2 \cdot MeI$ .—This substance, first prepared by O. Fischer and E. Tauber (*Ber.*, 1885, 18, 402) by the direct addition of methyl iodide to harmine, is conveniently obtained in the following manner. Harmin methosulphate (5 grams) dissolved in boiling water (150 c.c.) is mixed with boiling dilute potassium iodide (5 grams), when an immediate voluminous, almost colourless precipitate separates; this is collected and crystallised from alcohol, from which it separates in needles. When rapidly heated it darkens at 290° and melts at 305—307° to a black mass.

*Harmin Methochloride*,  $C_{13}H_{12}ON_2 \cdot MeCl$ .—This characteristic derivative is obtained when harmine methiodide, ground into a paste with much hot water, is digested on the steam-bath with a considerable excess of freshly prepared silver chloride. After filtering, the nearly colourless filtrate is concentrated and left overnight, when the liquid becomes filled with a mass of very pale yellow needles which exhibit a slight green fluorescence. The air-dry substance gave the following analytical results:

1.4307, heated at 100°, lost 0.2769.  $H_2O = 19.4$ .

\*0.1234 gave 0.2905  $CO_2$  and 0.0631  $H_2O$ .  $C = 64.2$ ;  $H = 5.7$ .

$C_{13}H_{12}ON_2 \cdot MeCl \cdot 4H_2O$  contains  $H_2O = 21.5$  and  $C_{13}H_{12}ON_2 \cdot MeCl$  requires  $C = 64.0$ ;  $H = 5.7$  per cent.

*Harmin methochloride*, when rapidly heated, scarcely darkens at 280° and melts at about 305° with effervescence to a black froth; it is rather sparingly soluble in boiling methyl alcohol and separates well in colourless groups of slender, prismatic needles. Its aqueous solution fluoresces blue and resembles the methosulphate in its behaviour with ammonia and sodium hydroxide.

#### *Methylharmine* (Formula XX or XXII).

This substance, first prepared by O. Fischer (*Ber.*, 1897, 30, 2482) from harmine methiodide by treatment with potassium hydr-

\* Dried at 100°.



oxide, is described as a colourless substance which melts at  $209^{\circ}$ , crystallises from benzene in needles, and rapidly absorbs carbon dioxide from the air. We have prepared methylharmine from harmine methosulphate and methochloride by the action of sodium hydroxide. The aqueous solution of either of these derivatives gives a voluminous, yellow precipitate on the addition of sodium hydroxide in the cold, and this is readily soluble in hot water and separates, on cooling slowly, in long, very pale yellow needles. After twice crystallising from water, the substance was left for three days exposed to the air and then analysed :

I. 1.1407, heated at  $100^{\circ}$ , lost 0.1999.  $H_2O = 17.5$ .

0.1033 gave 0.2350  $CO_2$  and 0.0668  $H_2O$ .  $C = 62.0$ ;  $H = 7.2$ .

$C_{14}H_{14}ON_2 \cdot 3H_2O$  requires  $H_2O = 19.3$ ;  $C = 60.0$ ;  $H = 7.1$  per cent.

II. Two specimens, heated at  $100^{\circ}$  until constant, gave the following analytical results :

0.1172 gave 0.3181  $CO_2$  and 0.0649  $H_2O$ .  $C = 74.0$ ;  $H = 6.2$ .

0.1286 „ 0.3506  $CO_2$  „ 0.0715  $H_2O$ .  $C = 74.3$ ;  $H = 6.3$ .

$C_{14}H_{14}ON_2$  requires  $C = 74.3$ ;  $H = 6.2$  per cent.

It is clear that the substance precipitated from harmine methosulphate or methochloride by sodium hydroxide is a hydrate of the probable composition,  $C_{14}H_{14}ON_2 \cdot 3H_2O$ , and that this loses all its water at  $100^{\circ}$ , leaving pure methylharmine which, as stated by Fischer, melts at  $209^{\circ}$ . The following experiment supports the view that the hydrate crystallised from water is harmine methohydroxide with  $2H_2O$ . When the hydrate is exposed over sulphuric acid in a vacuum desiccator it rapidly loses  $2H_2O$  and the last  $H_2O$  with much greater difficulty. Thus a specimen which had been exposed in the desiccator for six hours yielded  $C = 69.0$ ;  $H = 6.7$ ; after twenty-four hours it contained  $C = 70.8$ ;  $H = 6.4$ , and after two days  $C = 71.5$ ;  $H = 6.2$ , whereas  $C_{14}H_{14}ON_2 \cdot H_2O$  requires  $C = 68.8$ ;  $H = 6.4$  per cent.

Exposure to the air did not in our experience lead to the formation of carbonate as suggested by O. Fischer, since, after seven days' exposure, there was no effervescence on the addition of hydrochloric acid. Also analytical results are recorded above for air-dried material, and these were apparently not vitiated by absorption of carbon dioxide. *Methylharmine hydrochloride* is obtained as a sparingly soluble precipitate when the above hydrate is mixed with dilute hydrochloric acid. It crystallises from boiling dilute hydrochloric acid as a voluminous mass of needles, melts and decomposes at  $305^{\circ}$ , and is identical with harmine methochloride. (Found,  $C = 64.1$ ;  $H = 5.8$ .  $C_{14}H_{14}ON_2 \cdot HCl$  requires  $C = 64.0$ ;  $H = 5.7$  per cent.)

*Methylharmine Methosulphate*,  $C_{14}H_{14}ON_2Me_2SO_4$ .—Methylharmine reacts with methyl sulphate with the evolution of much heat and, in preparing the methosulphate, it is necessary either to employ small quantities of material or to use a diluent, such as benzene. When methylharmine (1 gram) is rubbed with methyl sulphate (1 c.c.), a stiff, chalky paste is soon formed and, after remaining overnight, the product is recrystallised from methyl alcohol, in which the methosulphate is unusually sparingly soluble and from which it separates as a voluminous mass of colourless needles:

0.1107 gave 0.2221  $CO_2$  and 0.0580  $H_2O$ .  $C=54.7$ ;  $H=5.8$ .

$C_{14}H_{14}ON_2Me_2SO_4$  requires  $C=54.6$ ;  $H=5.7$  per cent.

*Methylharmine methosulphate* is readily soluble in water and both the aqueous and methyl-alcoholic solutions, especially when dilute, exhibit a beautiful, pure blue fluorescence. It separates from a concentrated aqueous solution in felted needles. The solution in acetic acid gives, on the addition of sulphuric acid, a yellow liquid with a striking green fluorescence reminiscent of that of alkaline fluorescein; after a time the yellow colour and the fluorescence disappear, and the addition of a drop of dilute nitric acid produces a reddish-violet coloration. In concentrated sulphuric acid a similar fluorescent solution is obtained, and, on gently warming, this very rapidly fades and a colourless solution with violet fluorescence results. On the addition of water an extremely sparingly soluble precipitate consisting of colourless, satiny needles is formed. This substance contains sulphur, but differs from the sulphonic derivatives described on pp. 950, 953 in not being affected by aqueous sodium hydroxide even on boiling. The aqueous solution of the methosulphate is coloured yellow by potassium hydroxide, and, on heating to boiling, the yellow colour disappears, and if cooled much of the methosulphate separates unchanged. If, however, the boiling is continued for some time, a substance separates on cooling which appears to be the corresponding ammonium hydroxide. This was collected and dissolved in a large excess of boiling dilute hydrochloric acid, from which *methylharmine methochloride*,  $C_{14}H_{14}ON_2MeCl$ , separated as a voluminous mass of colourless needles:

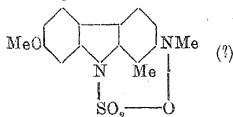
0.1108 gave 0.2631  $CO_2$  and 0.0615  $H_2O$ .  $C=64.8$ ;  $H=6.2$ .

$C_{14}H_{14}ON_2MeCl$  requires  $C=65.1$ ;  $H=6.7$  per cent.

This methochloride becomes yellow at  $270^\circ$  and melts at about  $280-285^\circ$  with effervescence to a reddish-brown syrup. The aqueous solution exhibits a fine blue fluorescence and becomes yellow on the addition of ammonia or sodium hydroxide, but no precipitate sepa-

rates. When, however, the aqueous solution, rendered strongly alkaline by sodium hydroxide, is boiled and concentrated, it deposits a pale yellow, crystalline precipitate, which dissolves in dilute hydrochloric acid with regeneration of the methochloride.

*Harmine Methohydroxide Sulphonic Anhydride,*



On one occasion, in preparing harmine methosulphate at  $100^{\circ}$  in an open vessel, it was noticed that instead of the expected product a very sparingly soluble, colourless substance was formed, and this result was traced to hydrolysis of the methyl sulphate and formation of sulphuric acid, which even under these conditions readily sulphonated the harmine methosulphate. It was then found that the same substance could be obtained by treating methylharmine in acetic anhydride with a few drops of sulphuric acid and by warming harmine methosulphate with concentrated sulphuric acid. A theoretical yield was obtained in the following manner. Harmine (5 grams) was finely powdered and heated during an hour on the steam-bath with toluene (20 c.c.) and methyl sulphate (15 c.c.), concentrated sulphuric acid (10 c.c.) was then added and the heating continued during half an hour. After the addition of water the precipitate was collected and dissolved in dilute sodium hydroxide. The filtered solution was diluted to 2000 c.c., heated to boiling, and acidified by the addition of hydrochloric acid. Almost immediately the substance crystallised from the solution in colourless, microscopic needles, which were collected, washed with hot water, and dried at  $100^{\circ}$ :

0.1301 gave 0.2629  $\text{CO}_2$  and 0.0545  $\text{H}_2\text{O}$ .  $\text{C}=55.1$ ;  $\text{H}=4.7$ .

0.1272 „ 0.0958  $\text{BaSO}_4$ .  $\text{S}=10.3$ .

$\text{C}_{14}\text{H}_{14}\text{O}_4\text{N}_2\text{S}$  requires  $\text{C}=54.9$ ;  $\text{H}=4.6$ ;  $\text{S}=10.5$  per cent.

This compound is very sparingly soluble in organic solvents and in water. It dissolves to some extent in boiling dilute hydrochloric acid and separates on cooling in an unchanged condition. Its solution in concentrated sulphuric acid is colourless, and exhibits a bluish-violet fluorescence. It is readily soluble in aqueous sodium hydroxide to a yellow solution, from which acids precipitate the original substance, but it is not attacked by cold sodium carbonate. A small quantity was boiled with dilute hydrochloric acid during

fourteen successive working days, when it was noticed that the amount which had separated, on cooling overnight, became smaller and smaller. On the addition of sodium hydroxide a precipitate was obtained, and this was collected and crystallised from benzene, when pale yellow needles of methylharmine melting at  $209^{\circ}$  were obtained. It is also possible to hydrolyse the substance with the formation of harmine. It slowly dissolved in boiling glycerol, and on pouring the solution into water only a small amount of insoluble material remained in suspension. The filtered liquid was mixed with sodium hydroxide, the precipitate collected and crystallised from alcohol. The colourless needles so obtained melted at  $256^{\circ}$  alone or when mixed with a specimen of pure harmine.

*Methylnorharmine* (Formula XIX).

Norharmine (2 grams) (Perkin and Robinson, T., 1912, 101, 1786) was dissolved in the minimum quantity of boiling benzene and methyl sulphate (5 c.c.) added to the solution, which was not again heated. The methosulphate soon separated as an oil, which later crystallised, and after leaving overnight the benzene was decanted and the solid washed with ether and then dissolved in water. The colourless solution exhibited blue fluorescence, and on the addition of an excess of sodium hydroxide a yellow, chalky precipitate was obtained. This was collected, dried in a vacuum desiccator over phosphoric oxide, and crystallised from dry benzene. The very pale yellow, flat needles melted at  $195\text{--}196^{\circ}$  with slight previous softening:

0.1049 gave 0.2832  $\text{CO}_2$  and 0.0549  $\text{H}_2\text{O}$ .  $\text{C}=73.6$ ;  $\text{H}=5.8$ .

$\text{C}_{13}\text{H}_{12}\text{ON}_2$  requires  $\text{C}=73.6$ ;  $\text{H}=5.7$  per cent.

*Methylnorharmine* is moderately readily soluble in alcohol, but sparingly so in benzene; it also dissolves in boiling water and crystallises on cooling, probably as norharmine methohydroxide. It has a great superficial resemblance to methylharmine, and dissolves in sulphuric acid to a similar yellow solution with bright green fluorescence. Its solutions in dilute aqueous acids exhibit a blue fluorescence.

*Harmaline Metho-salts.*

*Harmaline Methosulphate*,  $\text{C}_{13}\text{H}_{14}\text{ON}_2\cdot\text{Me}_2\text{SO}_4$ .—Harmaline combines more energetically with methyl sulphate than does harmine, and the methosulphate is readily prepared by rubbing harmaline (1 gram) with methyl sulphate (1 c.c.), when, even with such small quantities, a considerable rise of temperature will be observed.

After a few hours the yellow mass is crystallised from methyl alcohol, from which the methosulphate separates in yellow needles, and the mother liquor, on the addition of ether, gives a further crop of the same substance. Larger quantities are best prepared, in almost quantitative yield, under the following conditions. Finely powdered and sieved harmaline (30 grams) is covered with benzene (50 c.c.) and mixed with methyl sulphate (30 c.c.), when there is no immediate development of heat, but, on keeping, the temperature gradually rises to about  $40^{\circ}$ . After remaining for two days, the crystalline mass is collected, washed with benzene, and drained on porous porcelain; it is then pure enough for many purposes:

0.4332 gave 0.2989  $\text{BaSO}_4$ .  $S = 9.4$ .

$\text{C}_{13}\text{H}_{14}\text{ON}_2 \cdot \text{Me}_2\text{SO}_4$  requires  $S = 9.4$  per cent.

*Harmaline methosulphate* shrinks at  $160^{\circ}$  and melts at about  $170$ — $172^{\circ}$  to a deep yellow liquid; it is readily soluble in water or alcohol. The addition of sodium hydroxide to the cold concentrated aqueous solution gives a viscid, orange-red precipitate which, when washed free from alkali and boiled with water, becomes yellow and crystalline, and this substance appears to be nearly pure methylharmaline (compare O. Fischer, *Ber.*, 1897, **30**, 2484; 1914, **47**, 102). The boiling aqueous solution of the methosulphate gives, on the addition of potassium iodide, an immediate yellow, crystalline precipitate of the methiodide,  $\text{C}_{13}\text{H}_{14}\text{ON}_2 \cdot \text{MeI}$ . This method of preparation yields at once the pure methiodide, and is therefore to be preferred to the direct combination of harmaline with methyl iodide, since by this latter process dimethylharmaline iodide is also produced (O. Fischer, *Ber.*, 1914, **47**, 104).

*Harmaline Methochloride*,  $\text{C}_{13}\text{H}_{14}\text{ON}_2 \cdot \text{MeCl} \cdot 4\text{H}_2\text{O}$ .—This substance is readily prepared by digesting a paste of harmaline methiodide and much water with an excess of silver chloride on the steam-bath for a couple of hours and filtering. The filtrate is concentrated and allowed to cool slowly, when the methochloride separates as a crust of pale yellow, glistening prisms with a faint green lustre:

\*1.0380 lost 0.2223 in the steam-oven.  $\text{H}_2\text{O} = 21.6$ .

†0.1323 gave 0.3097  $\text{CO}_2$  and 0.0786  $\text{H}_2\text{O}$ .  $C = 63.9$ ;  $H = 6.6$ .

$\text{C}_{13}\text{H}_{14}\text{ON}_2 \cdot \text{MeCl} \cdot 4\text{H}_2\text{O}$  contains  $\text{H}_2\text{O} = 21.4$  and  $\text{C}_{13}\text{H}_{14}\text{ON}_2 \cdot \text{MeCl}$  requires  $C = 63.5$ ;  $H = 6.4$  per cent.

*Harmaline methochloride* begins to decompose at  $260^{\circ}$  and melts at about  $278^{\circ}$  with vigorous effervescence to a reddish-brown froth. It is very readily soluble in hot water or acetic acid, sparingly so in alcohol, and almost insoluble in boiling acetone. The aqueous

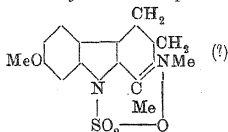
\* Air-dry.

† Dried at  $100^{\circ}$ .

solution is not precipitated by ammonia, and the bearing of this observation on the constitution of harmaline has been referred to on p. 940. Sodium hydroxide decomposes the salt in aqueous solution and produces an orange-red, viscid mass, which, when washed and boiled with water, becomes yellow and crystalline and doubtless consists of methylharmaline (see above).

The cold aqueous solution of the methochloride instantly decolorises permanganate.

*Harmaline Methohydroxide Sulphonic Anhydride,*



When finely divided harmaline methochloride is mixed with concentrated sulphuric acid, it dissolves to an orange-red solution with vigorous evolution of hydrogen chloride. If, after heating on the steam-bath for five minutes, water is added, a substance gradually separates as a voluminous mass of pale lemon-yellow needles. The compound is extremely sparingly soluble in water, but may be crystallised from much boiling water and obtained in long, lemon-yellow needles which become opaque and chalky in the steam-oven. It contains sulphur:

0.1050 gave 0.2108  $\text{CO}_2$  and 0.0494  $\text{H}_2\text{O}$ .  $\text{C}=54.7$ ;  $\text{H}=5.2$ .

$\text{C}_{14}\text{H}_{16}\text{O}_4\text{N}_2\text{S}$  requires  $\text{C}=54.5$ ;  $\text{H}=5.2$  per cent.

This substance is almost insoluble even in boiling acetic acid, it does not melt and scarcely shows any sign of decomposition at  $300^\circ$ . It is not soluble in cold aqueous sodium carbonate, but dissolves on the addition of a drop of sodium hydroxide to a yellow solution, and is precipitated unchanged by hydrochloric acid.

*Reduction of Harmaline Methosulphate or the Methochloride:*

*Formation of Methyltetrahydroharmine.*

In the first of these reductions, harmaline methosulphate (3 grams), dissolved in dilute sulphuric acid, was reduced in a porcelain beaker fitted with a mechanical stirrer with 3 per cent. sodium amalgam (200 grams), when the colour of the solution gradually faded and the process was completed by heating on the steam-bath. The filtered liquid, rendered alkaline by the addition

of sodium hydroxide, yielded a gummy mass, which soon hardened, and the solution in boiling methyl alcohol deposited, on cooling and stirring vigorously, a mass of glistening plates which, after recrystallisation, melted at 174—176°. This substance has the formula  $C_{14}H_{18}ON_2$  (Found, C=72·8; H=8·0; N=12·1.  $C_{14}H_{18}ON_2$  requires C=73·1; H=7·8; N=12·2 per cent.), and is evidently identical with the methyl dihydroharmaline which O. Fischer (*Ber.*, 1914, 47, 103) obtained from methylharmaline hydrochloride by reducing in amyl-alcoholic solution with sodium. In the second experiment, which appears to give the purer product, harmaline methochloride (5 grams), dissolved in water (300 c.c.) and hydrochloric acid (50 c.c.), was reduced on the steam-bath by the rapid addition of 3 per cent. sodium amalgam (250 grams). The yellow colour of the methochloride solution rapidly disappeared, and, on adding sodium hydroxide and crystallising the solid base from methyl alcohol, a crust of colourless prisms of methyltetrahydroharmine was obtained which melted directly at 176°.

*Methyltetrahydroharmine Methosulphate*,  $C_{14}H_{18}ON_2 \cdot Me_2SO_4$ .—When methyltetrahydroharmine (2 grams) is mixed with methyl sulphate (3 c.c.) it dissolves with considerable rise of temperature and the clear syrup suddenly crystallises. A rather better yield is obtained if the base is covered with benzene before mixing with methyl sulphate (see p. 946), when a syrup separates which rapidly crystallises.

The product is then recrystallised from methyl alcohol, in which it is readily soluble and from which it separates as a hard crust of well-developed, colourless prisms\* :

0·1049 gave 0·2054  $CO_2$  and 0·0655  $H_2O$ . C=53·4; H=6·9.

0·1181 „ 0·2327  $CO_2$  „ 0·0688  $H_2O$ . C=53·7; H=6·5.

$C_{16}H_{24}O_3N_2S$  requires C=54·0; H=6·7 per cent.

This methosulphate melts at about 188° without effervescence and is readily soluble in water, yielding a solution which has an extremely bitter taste.

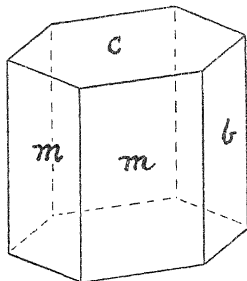
Crystals of methyltetrahydroharmine methosulphate were kindly examined by Miss M. W. Porter, who finds that they are monoclinic with  $a:b=0·738$ ,  $\beta=96°55'$ . The crystals are of a stout,

\* A considerable amount of methosulphate remains in the mother liquors and, if the methyl alcohol is removed by distillation from the steam-bath, most of this decomposes and is converted into a tar.

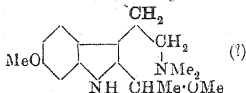
The best plan is to expose the mother liquor over sulphuric acid in a vacuum desiccator, when a hard crust gradually separates mixed with some tar; the latter can be removed by rubbing with cold methyl alcohol and leaving in contact with porous porcelain.

prismatic habit, as shown in Fig. 1, and exhibit the forms  $b(010)$ ,  $m(110)$ , and  $c(001)$ . The faces were somewhat curved. Following are the means of the two angles measured:  $m(\text{azimuth}) = 53^\circ 47'$ ,  $c(\text{polar distance}) = 6^\circ 55'$ .

FIG. 1.



*isoMethyltetrahydroharmine Methoxyhydroxide Methyl Ether,*



This substance, which is evidently identical with that obtained by O. Fischer (*Ber.*, 1914, **47**, 104) from the product of the action of methyl iodide on methyltetrahydroharmine by decomposition with methyl-alcoholic potassium hydroxide (compare p. 946), is readily prepared in the following manner: Methyltetrahydroharmine methosulphate (1 gram), dissolved in a little boiling methyl alcohol, is mixed with methyl-alcoholic potassium hydroxide (10 c.c. of 25 per cent.) and boiled for half an hour. Most of the methyl alcohol is then evaporated under reduced pressure and water added, when an oil separates which soon crystallises. The substance is readily purified by recrystallisation from ether, when it separates as a mass of colourless needles or from a mixture of benzene and light petroleum, from which it crystallises in flat needles. In view of the fact that this substance appeared to have a composition different from that ( $C_{15}H_{22}O_2N_2$ ) assigned to it by O. Fischer (*loc. cit.*, compare p. 945), it became necessary to carry out several analyses. The following were made with three different preparations, the first



two having been twice recrystallised from ether and the third from benzene and light petroleum in addition :

- I. 0.1067 gave 0.2733  $\text{CO}_2$  and 0.0840  $\text{H}_2\text{O}$ .  $\text{C}=69.8$ ;  $\text{H}=8.7$ .  
 0.2093 „ 18.7 c.c.  $\text{N}_2$  at  $11.5^\circ$  and 732 mm.  $\text{N}=10.2$ .  
 II. 0.1059 „ 0.2705  $\text{CO}_2$  and 0.0829  $\text{H}_2\text{O}$ .  $\text{C}=69.7$ ;  $\text{H}=8.7$ .  
 III. 0.1214 „ 0.3102  $\text{CO}_2$  „ 0.0953  $\text{H}_2\text{O}$ .  $\text{C}=69.7$ ;  $\text{H}=8.7$ .  
 $\text{C}_{16}\text{H}_{24}\text{O}_2\text{N}_2$  requires  $\text{C}=69.6$ ;  $\text{H}=8.7$ ;  $\text{N}=10.1$  per cent.  
 $\text{C}_{15}\text{H}_{22}\text{O}_2\text{N}_2$  „  $\text{C}=68.7$ ;  $\text{H}=8.4$ ;  $\text{N}=10.7$  „ „

The analytical results given by O. Fischer are  $\text{C}=69.1$  and  $69.0$ ;  $\text{H}=8.78$  and  $8.67$ ; and  $\text{N}=10.81$ .

A methoxyl determination by Zeisel's method yielded the following result:

0.2865 gave 0.4790  $\text{AgI}$ .  $\text{MeO}=22.1$ .

$\text{C}_{16}\text{H}_{24}\text{O}_2\text{N}_2$ , containing 2 $\text{MeO}$ , requires  $\text{MeO}=22.4$  per cent.

*isoMethyltetrahydroarmine methohydroxide methyl ether* melts at  $123$ — $129^\circ$  and is readily soluble in alcohol, acetone, or benzene, but sparingly so in water, ether, or light petroleum. It crystallises from dilute methyl alcohol in large, colourless plates or from much light petroleum in groups of flat needles. When it is heated in small quantities it distils with only slight decomposition, but, under 10 mm. pressure, it passes over without residue as a colourless syrup which, when rubbed, solidifies completely. After washing with ether on porous porcelain, the colourless, crystalline mass melted at  $121$ — $126^\circ$  and the admixture with the original substance at  $123$ — $126^\circ$ , showing that no change, such as elimination of water, had taken place during the distillation.

*isoMethyltetrahydroarmine Methohydroxide Ethyl Ether*,  $\text{C}_{17}\text{H}_{26}\text{O}_2\text{N}_2$ .—In order to confirm the composition given for the product of the action of methyl alcohol on methyltetrahydroarmine methosulphate, the latter substance (1 gram) was digested with ethyl-alcoholic potassium hydroxide (10 c.c. of 20 per cent.) for an hour. On adding water, a viscid, ochreous precipitate separated, which was extracted with ether, and the ethereal solution, after thoroughly washing and drying over potassium carbonate, concentrated and left in the ice-chest for a week, but nothing separated.

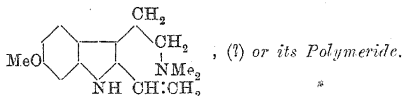
The ether was then allowed to evaporate slowly over sulphuric acid, when a pasty mass of crystals remained, which was left in contact with porous porcelain until quite dry and hard. As all attempts to recrystallise this substance were unsuccessful, it was dried over phosphoric oxide and analysed:

0.1399 gave 0.3614  $\text{CO}_2$  and 0.1116  $\text{H}_2\text{O}$ .  $\text{C}=70.4$ ;  $\text{H}=8.8$ .

$\text{C}_{17}\text{H}_{26}\text{O}_2\text{N}_2$  requires  $\text{C}=70.3$ ;  $\text{H}=9.0$  per cent.

When treated with hydrochloric acid and then with potassium iodide, this substance yields a hydrochloride,  $C_{15}H_{20}ON_2.HCl$ , and hydriodide,  $C_{15}H_{20}ON_2.HI$  (m. p. 290—295°), identical with those produced under the same conditions from *isomethyltetrahydroharmine methohydroxide methyl ether* (see below).

*Dehydroisomethyltetrahydroharmine Methohydroxide,*



The *hydrochloride*,  $C_{15}H_{20}ON_2.HCl$ , of this base is obtained when *isomethyltetrahydroharmine methohydroxide methyl ether* is treated with dilute hydrochloric acid. The methyl ether dissolves in cold dilute hydrochloric acid, and almost immediately the solution clouds and a caseous substance separates, which soon hardens. This curious salt melts under hot water, dissolves to a pale violet solution, and the addition of hydrochloric acid causes a very pale blue, apparently crystalline, precipitate to separate, which was collected, washed with dilute hydrochloric acid, and dried on porous porcelain over solid potassium hydroxide and then in the steam-oven:

0.1032 gave 0.2415  $CO_2$  and 0.0707  $H_2O$ .  $C=63.8$ ;  $H=7.6$ .

$C_{15}H_{20}ON_2.HCl$  requires  $C=64.2$ ;  $H=7.5$  per cent.

This hydrochloride is readily soluble in water, but sparingly so in dilute hydrochloric acid; the aqueous solution gives on the addition of platinic chloride a pale brown precipitate, which on warming becomes black, and with auric chloride a drab precipitate which becomes violet on heating owing to the separation of metallic gold. When ammonia is added to the solution of the hydrochloride a nearly colourless jelly separates, which is evidently the free dehydro-base (see below).

The *Hydriodide*,  $C_{15}H_{20}ON_2.HI$ .—The methyl ether dissolves in dilute sulphuric acid at 40°, and, on keeping, the solution clouds and deposits a caseous precipitate of the sulphate, which gradually becomes crystalline.

This was collected, dissolved in warm water, and mixed with potassium iodide, when a sparingly soluble, amorphous precipitate separated, which also became crystalline on warming. After washing well and drying in the steam-oven, this hydriodide was analysed:

0.1089 gave 0.1954  $\text{CO}_2$  and 0.0567  $\text{H}_2\text{O}$ .  $\text{C}=49.0$ ;  $\text{H}=5.8$ .

$\text{C}_{15}\text{H}_{20}\text{ON}_2\cdot\text{HI}$  requires  $\text{C}=48.7$ ;  $\text{H}=5.6$  per cent.

On heating in a capillary tube this iodide remains nearly colourless until  $250^\circ$ , then gradually becomes brown, and melts at about  $290$ — $295^\circ$  with vigorous decomposition to a black froth.

*Dehydroisomethyltetrahydroharmine methohydroxide* was obtained by rubbing the hydriodide to a fine paste with a large excess of dilute ammonia, and, after remaining overnight, the ochreous precipitate was collected and digested at about  $60^\circ$  with a further quantity of dilute ammonia, the process being repeated until no more iodine was removed. The pale ochreous precipitate was collected, thoroughly washed with dilute ammonia, and dried first in a desiccator over phosphoric oxide and then in the steam-oven:

0.1184 gave 0.3182  $\text{CO}_2$  and 0.0874  $\text{H}_2\text{O}$ .  $\text{C}=73.3$ ;  $\text{H}=8.2$ .

$\text{C}_{15}\text{H}_{20}\text{ON}_2$  requires  $\text{C}=73.8$ ;  $\text{H}=8.2$  per cent.

This curious substance does not melt, and indeed scarcely darkens, at  $300^\circ$ ; it dissolves very readily in methyl alcohol, and is precipitated as a pale ochreous precipitate on the addition of ether, but it has not so far been possible to obtain it in a definitely crystalline condition.

Boiling with dilute hydrochloric acid converts it into a sparingly soluble hydrochloride; it dissolves, however, readily in warm glacial acetic acid, yielding a colourless solution which is not precipitated by water. On the addition of ammonia, a colloidal solution is obtained which, on boiling, deposits a flocculent, gelatinous precipitate consisting apparently of the dehydro-base.

The *Methosulphate* and the *Methiodide*,  $\text{C}_{15}\text{H}_{20}\text{ON}_2\cdot\text{MeI}$ .—The solution of *isomethyltetrahydroharmine methohydroxide* methyl ether (1 gram) in benzene (5 c.c.) gives, on the addition of methyl sulphate (1 c.c.), a cloudy liquid: there is considerable development of heat, and a gum separates which is evidently the methosulphate of the dehydro-base. The benzene was decanted, the gum washed with ether, dissolved in hot water and mixed with potassium iodide, when a jelly separated which, on warming, became granular:

0.1147 gave 0.2097  $\text{CO}_2$  and 0.0601  $\text{H}_2\text{O}$ .  $\text{C}=49.9$ ;  $\text{H}=5.8$ .

$\text{C}_{15}\text{H}_{20}\text{ON}_2\cdot\text{MeI}$  requires  $\text{C}=49.8$ ;  $\text{H}=5.9$  per cent.

This methiodide does not darken until  $260^\circ$ , and melts at about  $290$ — $292^\circ$  with effervescence to a black froth.

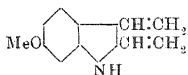
The methosulphate behaves in a remarkable manner when its solution in methyl alcohol is boiled with methyl-alcoholic potassium hydroxide.

Trimethylamine is eliminated but with difficulty, and, on adding water, a milky liquid is produced which gradually deposits a con-

siderable rather viscid precipitate. This was collected and found to be almost insoluble in the usual organic solvents and, after it had been boiled with methyl alcohol, ether, benzene, and finally acetone, a grey mass remained which was exactly similar to india-rubber in appearance and many of its properties.

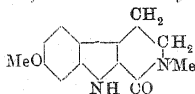
It was resilient like rubber, frothed up on heating to a high temperature, and was quite insoluble in acetic or dilute hydrochloric acid.

There can be little doubt that this mass is a polymeric modification of the divinyl derivative:



but the substance was not further investigated.

*Oxidation of Methyltetrahydroharmine and of Harmaline Methosulphate: Formation of Ketoisonormethyltetrahydroharmine,*



In studying the oxidation of methyltetrahydroharmine, the base (5 grams), dissolved in acetone (250 c.c.), was gradually treated with very finely powdered permanganate (11 grams) at  $-10^{\circ}$ . When the decolorisation of the permanganate, which took place very slowly, was complete the product was filtered, the manganese precipitate thoroughly washed with acetone (A), extracted with boiling water, and the dark brown extract concentrated. On neutralising with acetic acid, precipitating with lead acetate, and decomposing the small amount of lead salt with hydrogen sulphide, only 0.5 gram of a dark, resinous acid was obtained, from which nothing crystalline could be isolated. The acetone filtrate (A) was concentrated considerably and allowed to remain in the ice-chest, when a heavy, crystalline precipitate rapidly separated, which was collected and washed with methyl alcohol, in which it is almost insoluble.

The substance dissolves in much boiling acetone and separates, on cooling, in glistening, pale lemon-yellow needles:

0.1012 gave 0.2498  $\text{CO}_2$  and 0.0555  $\text{H}_2\text{O}$ .  $\text{C}=67.3$   $\text{H}=6.1$ .

0.1113 „ 0.2769  $\text{CO}_2$  „ 0.0619  $\text{H}_2\text{O}$ .  $\text{C}=67.8$ ;  $\text{H}=6.1$ .

$\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2$  requires  $\text{C}=67.8$ ;  $\text{H}=6.1$  per cent.

*Ketoisonormethyltetrahydroharmine* melts at  $228^{\circ}$  and is sparingly soluble in the usual organic solvents. It does not dissolve in dilute mineral acids, and its solution in glacial acetic acid is precipitated by water. Concentrated sulphuric acid dissolves the substance readily to a yellowish-brown solution, but, even after heating on the steam-bath for some minutes, water precipitates much unchanged substance. It is insoluble in cold concentrated hydrochloric acid, but when boiled with the acid it partly dissolves and a crystalline substance separates, which appears to be the hydrochloride and is immediately dissociated on the addition of water. It is also insoluble in aqueous alkalis and in cold methyl-alcoholic potassium hydroxide, but it dissolves in the latter on boiling and crystallises unchanged when the solution is cooled.

*Behaviour of Ketoisonormethyltetrahydroharmine with Phosphoryl Chloride and Pentachloride.*—That this substance is not readily attacked by these reagents is shown by the following experiment.

When the substance (1 gram) is warmed with phosphoryl chloride (1.5) it is converted into a voluminous, yellow mass consisting probably of the hydrochloride, and if powdered phosphorus pentachloride is now added and the whole heated on the steam-bath a clear liquid is produced.

After heating for fifteen minutes the yellow liquid was poured on powdered ice, when a deep orange, viscid precipitate separated, which was collected, drained on porous porcelain, and rubbed with cold methyl alcohol.

This removes the viscid impurity and leaves a pale ochreous powder, which, after contact with porous porcelain and again washing with methyl alcohol, weighed 0.6 gram, melted at  $225-228^{\circ}$ , and consisted of unchanged substance.

If the experiment is conducted at a higher temperature than that of the steam-bath some profound change occurs, but the matter has not been further investigated.

*Oxidation of Harmaline Methosulphate.*—This methosulphate is somewhat sparingly soluble in acetone, even on boiling, and separates in short, well-developed, glistening prisms with bevelled edges. For the purpose of oxidation, the methosulphate (1.5 grams) was dissolved in the least possible quantity of boiling water, mixed with acetone (40 c.c.), and cooled to  $-10^{\circ}$ , during which some of the methosulphate separated in a very finely divided condition. Powdered permanganate (2.3 grams) was then gradually added, and so soon as oxidation was complete the whole was filtered and the precipitate, which yields only a trace of acid on extraction with water and acidifying, washed thoroughly with warm acetone. On concen-

trating the acetone extract on the steam-bath, a crystalline mass (0.4 gram) separated which, after recrystallisation from acetone, melted at  $227^{\circ}$  and consisted of keto*iso*normethyltetrahydroharmine. (Found,  $C=67.9$ ;  $H=6.1$ .  $C_{13}H_{14}O_2N_2$  requires  $C=67.8$ ;  $H=6.1$  per cent.)

*Reduction of Harmaline to Tetrahydroharmine.*

Tetrahydroharmine,  $C_{13}H_{16}ON_2$  (m. p.  $199^{\circ}$ ), was first prepared by O. Fischer (*Ber.*, 1889, **22**, 637) by the reduction either of harmine or harmaline in alcoholic solution by sodium and later (*Ber.*, 1897, **30**, 2484) in *iso*amyl alcohol solution by sodium. We find that it may be readily prepared by the following simple process: Harmaline (5 grams), dissolved in water (100 c.c.) and hydrochloric acid (20 c.c.), is heated to boiling and then sodium amalgam (300 grams of 3 per cent.) added in three portions, together with further small quantities of hydrochloric acid, so that the liquid is always strongly acid. The deep yellow colour of the harmaline hydrochloride gradually disappears and the solution at the end is almost colourless. On cooling, the sparingly soluble hydrochloride of tetrahydroharmine separates in colourless crusts, and this is collected, dissolved in hot water, precipitated by ammonia, and the base crystallised from methyl alcohol, from which it separates in bundles of needles melting at  $198-199^{\circ}$ . (Found,  $C=72.3$ ;  $H=7.6$ .  $C_{13}H_{16}ON_2$  requires  $C=72.2$ ;  $H=7.4$  per cent.) A further quantity may be obtained from the original mother liquors of the hydrochloride, and the total yield is about 90 per cent. of that theoretically possible.

*Oxidation of Tetrahydroharmine to Harmaline.*—In this experiment tetrahydroharmine (2 grams), dissolved in acetone (150 c.c.), was cooled to  $-10^{\circ}$  and then oxidised by the gradual addition of very finely powdered permanganate (4 grams). The oxidation takes place very gradually, and as soon as the permanganate has been completely decolorised, the whole is filtered and the acetone filtrate concentrated to a small bulk, when a mass of crystals separates which melt at  $245^{\circ}$  and consist of harmaline, as a mixed melting point and careful comparison of properties clearly demonstrated. (Found,  $C=73.2$ ;  $H=6.6$ .  $C_{13}H_{14}ON_2$  requires  $C=72.9$ ;  $H=6.6$  per cent.)

*Conversion of Tetrahydroharmine into Methyltetrahydroharmine*  
(m. p.  $176^{\circ}$ ).

The methylation of tetrahydroharmine takes place readily under the following conditions: Tetrahydroharmine (3 grams), suspended

in benzene (10 c.c.), is stirred with methyl sulphate (3 c.c.), causing a considerable rise of temperature and separation of a syrup which consists mainly of the methyl hydrogen sulphate of methyltetrahydroharmine.

After twenty-four hours the benzene is decanted, the syrup rubbed and washed with ether, during which it becomes very viscid and stringy, but does not crystallise. This syrup, which contains some tetrahydroharmine methyl hydrogen sulphate or sulphate, was dissolved in water, in which it is very soluble, and mixed with ammonia, when a syrup separated which gradually crystallised. This was collected, dissolved in boiling methyl alcohol, cooled, and vigorously stirred, causing an appreciable amount (about 0.3 gram) of tetrahydroharmine to separate, which was removed by filtration.

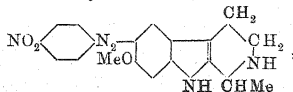
The filtrate was allowed to evaporate and the residual pale brown syrup rubbed with a few drops of methyl alcohol, when it soon began to crystallise and, after remaining in contact with porous porcelain and recrystallisation first from benzene and then from methyl alcohol, a colourless mass of needles was obtained which melted at  $174-176^{\circ}$ , and consisted of methyltetrahydroharmine (Found: C=73.3; H=7.9.  $C_{14}H_{18}ON_2$  requires C=73.1; H=7.8 per cent.).

#### *The Behaviour of Harmine Derivatives with Diazonium Salts.*

Harmine, harmine methosulphate, methylharmine, methylharmine methosulphate, methylharminesulphonic acid, norharmine, and methylnorharmine do not react with benzenediazonium chloride, *p*-nitrobenzenediazonium chloride, or diazobenzenesulphonic acid in aqueous acid, alkaline, or neutral solution. O. Fischer and Boesler (*loc. cit.*) have shown that harmaline forms bisazo-derivatives, and for the sake of comparison with *p*-nitrobenzeneazotetrahydroharmine we prepared the condensation products from harmaline and harmaline methochloride with *p*-nitrobenzenediazonium chloride in dilute acetic acid solution in the presence of sodium acetate. Harmaline gave a dark chocolate-brown precipitate, which appeared slowly and dissolved in concentrated sulphuric acid to a fine, intense royal-blue solution, which, on keeping, became successively dull reddish-purple, reddish-brown, and brown. Harmaline methochloride under similar conditions gave an almost black precipitate, which dissolved in sulphuric acid to a blue solution which, on keeping, became bluish-green, olive-green, and finally dull brown. Methylharmalinesulphonic acid (or harmaline-methohydroxide-sulphonic anhydride) also condenses

with diazonium salts in alkaline solution, and with tetrazotised benzidine yields a dull reddish-purple solution with very deep green fluorescence. On the addition of acid, the solution becomes orange-yellow and the fluorescence disappears, but the alkaline solution dyes cotton in dull mauve shades unaffected by acid. Tetrahydroharmine and *N*-methyltetrahydroharmine condense immediately with diazonium salts in acetic acid solution. With tetrazotised benzidine either of these bases gives a bright red precipitate which dissolves in dilute hydrochloric acid to a reddish-purple, bluish-purple, or pure blue solution according to the concentration of the acid. In concentrated sulphuric acid the solution is pure blue. A dilute acid solution dyes cotton in intermediate shades. The dyed fabric becomes blue if placed in moderately concentrated hydrochloric acid, and on washing with water the colour changes to terra-cotta. Cotton is also dyed terra-cotta by an alcoholic solution of the azo-derivative. With simple benzenediazonium salts, tetrahydroharmine gives yellow to orange precipitates, whilst with those derived from naphthylamines the colour is usually red.

*p*-Nitrobenzeneazotetrahydroharmine,



is obtained as a reddish-brown precipitate on the addition of a solution of *p*-nitrobenzenediazonium acetate to an aqueous acetic acid solution of tetrahydroharmine. Tetrahydroharmine (0.216 gram) was dissolved in water (10 c.c.) and acetic acid (2 c.c.). *p*-Nitroaniline (0.272 gram: 2 mols.) was dissolved in warm concentrated hydrochloric acid (3 c.c.), diluted with water (10 c.c.), and diazotised by the addition of sodium nitrite, after which the solution was made up to 25 c.c. by the addition of saturated aqueous sodium acetate solution. One half exactly of the diazotised *p*-nitroaniline solution was then added to the tetrahydroharmine solution, and after one minute the precipitate was collected, thoroughly washed with water, dried at 100° and in a vacuum over phosphoric oxide until constant. The amount obtained was 0.340 gram, which is a yield of 93 per cent. of the theoretical. The filtrate contained no diazonium salt and, on the addition of the second half of the diazotised *p*-nitroaniline, there was a small precipitation of azo-derivative, but on adding an amount of tetrahydroharmine, dissolved in dilute acetic acid, judged to be approximately 0.2 gram, there was a voluminous precipitate. This experiment proves that the condensation occurs between one molecule of the base and one



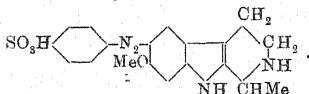
of the diazonium salt. The substance is soluble in boiling alcohol to a crimson solution and, on allowing to cool slowly, the greater part separated in an unsatisfactory condition, but the black powder was mixed with some long, coal-black needles which formed aggregates that could be separated mechanically. These were dried in a vacuum over sulphuric acid and analysed:

0.1147 gave 0.2638  $\text{CO}_2$  and 0.0554  $\text{H}_2\text{O}$ .  $\text{C}=62.7$ ;  $\text{H}=5.4$ .

$\text{C}_{19}\text{H}_{19}\text{O}_3\text{N}_5$  requires  $\text{C}=62.5$ ;  $\text{H}=5.2$  per cent.

*p*-Nitrobenzeneazotetrahydroharmine melts at  $173\text{--}175^\circ$  with decomposition to a black froth. It dissolves in concentrated hydrochloric acid to a crimson solution which becomes orange-red when greatly diluted with water. Unlike the nitrobenzeneazo-derivatives from harmaline and methylharmaline, the solution in sulphuric acid is carmine and does not change appreciably on allowing to remain. The black needles give a chocolate smear on paper, and this exhibits a beetle-green lustre. Methyltetrahydroharmine yields a very similar substance on coupling with diazotised *p*-nitroaniline, whilst methyltetrahydroharmine methosulphate in dilute acetic acid solution in the presence of sodium acetate yields an orange-red solution on the addition of *p*-nitrobenzenediazonium acetate, and this solution becomes blood-red on making alkaline with sodium hydroxide. The base, melting at  $129^\circ$ , obtained from the latter methosulphate by the action of alcoholic potassium hydroxide (p. 956), yields in acetic acid solution an orange-red liquid which becomes carmine on the addition of hydrochloric acid.

*Benzeneazotetrahydroharminesulphonic Acid,*



Tetrahydroharmine (1 gram) in dilute acetic acid (100 c.c.) was mixed with a solution of diazobenzenesulphonic acid (from 1 gram of sulphanilic acid) when an orange liquid was obtained, and in a few minutes an orange-yellow azo-compound separated in glistening, microscopic prisms. The substance was collected and purified by solution in dilute aqueous sodium hydroxide and precipitation by the addition of acetic acid. The crystals were collected, washed with water, and dried at  $100^\circ$ :

0.2860 gave 0.1658  $\text{BaSO}_4$ .  $\text{S}=8.0$ .

$\text{C}_{19}\text{H}_{20}\text{O}_4\text{N}_4\text{S}$  requires  $\text{S}=8.0$  per cent.

The substance is not soluble in cold sodium carbonate solution and is very sparingly soluble in organic solvents even in boiling glacial acetic acid. It dissolves in aqueous sodium hydroxide to a bright orange-yellow solution, and this becomes crimson on the addition of hydrochloric acid. The change is very similar to that which is exhibited by methyl-orange when treated in a similar manner, but the harmine derivative gives a more intense coloration. It is, however, not so sensitive an indicator as methyl-orange and requires a higher concentration of hydrogen ion in order to effect the change of colour. A crimson acid solution was diluted with water until the colour had become orange-brown, and on the addition of a trace of methyl-orange the crimson colour was restored. Silk and wool are dyed in pale yellow shades from a suspension of this substance in hot dilute acetic acid.

*Benzeneazomethyltetrahydroharmine-sulphonic Acid.*

This substance was prepared from methyltetrahydroharmine in exactly the same way as described above for the corresponding tetrahydroharmine derivatives. The only difference noted was that it crystallised more slowly from solution and had a reddish-brown colour. In acid and alkali it behaved exactly as the substance just described:

0.3142 gave 0.1787 BaSO<sub>4</sub>. S=7.7.

C<sub>20</sub>H<sub>22</sub>O<sub>4</sub>N<sub>4</sub>S requires S=7.8 per cent.

It is an interesting circumstance that the basic nitrogen atom of tetrahydroharmine is not concerned in the coupling with diazonium salts, and this follows from the observation that *N*-acetyl tetrahydroharmine, which does not dissolve in dilute acids, condenses with diazobenzenesulphonic acid in aqueous acetic acid solution with the formation of an azo-derivative which is crimson in acid and yellow in alkaline solutions. The oxidation product of harmaline methosulphate, ketoisonormethyltetrahydroharmine (m. p. 228°, p. 960), does not condense with diazonium salts.

*Colour Reactions for Indole Derivatives applied to Degradation Products of Harmine.*

O. Fischer (*Ber.*, 1897, **30**, 2484) noted that tetrahydroharmine colours a pine shaving green in hydrochloric acid solution and that dihydroapoharmine (*Ber.*, 1889, **22**, 640) under the same conditions produces an orange colour, but these reactions are not very

characteristic, and we have tried to obtain more definite evidence that harmine is an indole derivative. Almost all the hydro-derivatives give indole indications after fusion with potassium hydroxide, but we specifically mention only those examples which are characteristic. Ketoisomethyltetrahydroharmine (m. p. 228°, p. 960), obtained by the oxidation of harmaline methosulphate, is very stable towards fusion with potassium hydroxide, and remains for some time as a yellow or yellowish-brown oil. At a certain point the mixture froths and becomes almost homogeneous and the reaction is then finished. Water is added and the liquid extracted with ether. The colourless, ethereal solution is washed with dilute hydrochloric acid and evaporated, when a small residue is obtained, and this colours a wood shaving blue, in alcoholic hydrochloric acid solution, and gives a deep blue coloration with *p*-dimethylaminobenzaldehyde and aqueous-alcoholic hydrochloric acid on gently warming. The ethereal solution evidently contained a neutral indole derivative, and this was confirmed by treating another portion with concentrated hydrochloric acid and vanillin, when a crimson solution was obtained. Still another portion was dissolved in sulphuric acid to an orange-red solution, which on the addition of a trace of glyoxylic acid (obtained by adding magnesium powder to a concentrated aqueous solution of oxalic acid) became brownish-purple. The hydrochloric acid washings of the ethereal extract were rendered alkaline with sodium hydroxide and extracted with ether. After removal of the solvent the colour reactions just described could be obtained. The fusion of the substance melting at 228°, with potassium hydroxide, results, therefore, in the production of a basic and a neutral indole derivative. The colour obtained with *p*-dimethylaminobenzaldehyde indicates that an  $\alpha$ -position has been set free in the indole ring, since scatole gives a blue coloration with this reagent, whilst  $\alpha$ -methylindole gives a crimson colour and its methylenedioxy-derivative (Foulds and Robinson, T., 1914, 105, 1969) almost an identical shade, showing that alkyloxy-groups in the ring are not likely to modify these colour reactions to any great extent. When isomethyltetrahydroharmine methohydroxide methyl ether (m. p. 129°, p. 956), obtained from methyltetrahydroharmine methosulphate by the action of methyl-alcoholic potassium hydroxide, is fused with alkali in the presence of air at a high temperature and the product subsequently treated with water, acidified, and the solution evaporated to dryness, a mauve-red coloration is obtained in the test with *p*-dimethylaminobenzaldehyde. This indicates the production of an indole derivative with a free  $\beta$ -position. The base, melting at

129°, and also *N*-acetyltetrahydroharmine yield, beyond question, indole derivatives when warmed with concentrated hydrochloric acid. The acetyl derivative gives a deep greenish-blue coloration when heated with hydrochloric acid and then mixed with an alcoholic solution of *p*-dimethylaminobenzaldehyde.

Either compound when heated with concentrated hydrochloric acid for thirty seconds and then treated with a little vanillin gives a most intense permanganate-coloured solution and, on the addition of water, a purple precipitate. Tetrahydroharmine itself gives a somewhat similar, but far weaker, reaction and a colourless substance separates. On adding water the latter remains unchanged, but most of the colour of the liquid is discharged. With vanillin and hydrochloric acid,  $\alpha$ -methylindole gives an orange colour and  $\beta$ -methylindole a blue solution.

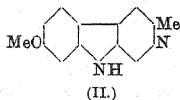
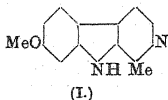
UNIVERSITIES OF OXFORD AND LIVERPOOL.

[Received, June 23rd, 1919.]

## LXXX.—*Harmine and Harmaline. Part IV.*

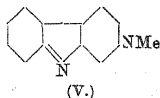
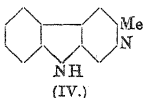
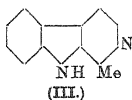
By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

IN Part III. of this research (this vol., p. 937) it was argued that harmine must be represented by one of the formulæ I or II, and evidence was brought forward which was interpreted in favour of the first of these alternatives:

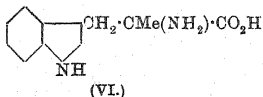


The corresponding expressions for the base, harman, which O. Fischer (*Chem. Centr.*, 1901, i, 957) obtained by eliminating the methoxyl group from harmine are III and IV respectively. In the communication already quoted (p. 945) the present authors also considered the question of the probable nature of a base,  $C_{12}H_{10}N_2$ , prepared by Hopkins and Cole (*J. Physiol.*, 1903, **29**, 451) from

tryptophan by oxidation with ferric chloride, and suggested the representations III and V, of which the former was preferred :

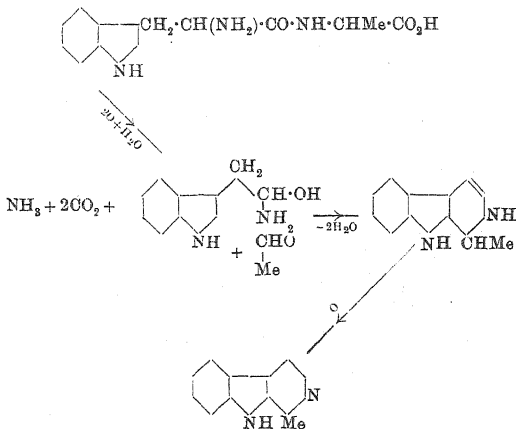


The possibility was therefore mooted that the base,  $C_{12}H_{10}N_2$  (m. p.  $238^\circ$ ), might prove to be harman (m. p.  $230^\circ$  according to O. Fischer, *loc. cit.*), and we are now able to state that this is actually the case. We are greatly indebted to Professor F. Gowland Hopkins, F.R.S., for a specimen of the base,  $C_{12}H_{10}N_2$ , and, as the result of a careful comparison, we can detect no difference between this substance and harman, the melting point of which we find is also  $238^\circ$ . The details are given in the brief experimental portion appended, and some of the theoretical consequences of this interesting result may now be considered. In the first place this conjunction of the chemistry of harmine and of tryptophan very much strengthens the case for acceptance of the formula I as the best summary of the relations of harmine, since it is almost inconceivable that a substance constituted as IV could arise from tryptophan, even in the presence of other substances. The only loophole is the possible occurrence in some specimens of this amino-acid of a methyltryptophan (VI), which is extremely improbable :

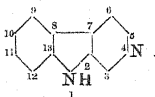


Secondly, the theory put forward in our preceding memoir (*loc. cit.*, p. 944) that harmine originates in nature from a hydroxy-tryptophan receives important confirmation, since harman may now be so simply obtained from tryptophan in the laboratory. Clearly the mechanism of the latter reaction is a matter worthy of close investigation, since it is probably on analogous lines to the vital synthesis of an alkaloïd. One possibility is expressed in the following scheme, in which tryptophan alone is supposed to yield the base and in which the unusual fission, occurring at the point indicated by the dotted line, may find some analogy in the decomposition of tryptophan by *B. coli* resulting in the formation of indole without scatole :

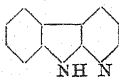




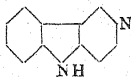
the name 'carboline'\* for this structure, indicating an analogy both to carbazole and quinoline. There are four carboline substitution products and these may be named in accordance with a scheme of numbering which is the same in all cases, and is indicated below in the case of 4-carboline (*norharman*):



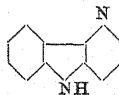
4-Carboline.



3-Carboline.



5-Carboline.

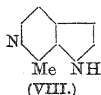
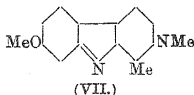


6-Carboline.

Isomeric and probably tautomeric with these are the four 'isocarbolines,' the numbering of which need not differ from that of the carbolines. Thus harmine is 11-methoxy-3-methyl-4-carboline,

\* The term "carbazoline" has already been used to denote reduction products of carbazole (compare Carrasco, *Gazzetta*, 1908, 38, ii, 301).

whilst methylharmine (VII, compare this vol., p. 942) is 11-methoxy-3:4-dimethyl-4-isocarboline:



*apo*Harmine, it may be pointed out, has now been shown to be 8-methyl-7-pyrindole (VIII) in accordance with the nomenclature previously suggested (T., 1912, 101, 1787) for fused pyrrole-pyridine nuclei.

#### EXPERIMENTAL.

O. Fischer (*loc. cit.*) converted harmine into the corresponding phenol, harmol, by demethylation with concentrated hydrochloric acid in a sealed tube at 140—170°. We have employed this method also, but, in addition, have prepared harmol in almost theoretical yield by boiling harmine with an excess of hydriodic acid (D 1·7) during five hours. On dilution with water and the addition of enough sulphurous acid to remove the free iodine, a crystalline precipitate remained and this was collected and dissolved in dilute aqueous sodium hydroxide. The filtered solution was acidified with acetic acid and the harmol precipitated by the addition of ammonia. The base was at first somewhat viscid, but very soon became granular and crystalline, and was then collected, washed with water, and dried at 100°. Harmol may be converted into harman by careful distillation with a very large excess of zinc dust in a stream of hydrogen, but owing to the high melting point of harmol the yield is unsatisfactory. The crude product from the distillation of 15 grams of harmol, intimately mixed with 250 grams of zinc dust, was dissolved in the minimum of cold concentrated sulphuric acid and the diluted solution mixed with insufficient aqueous ammonia to neutralise the acid. The sparingly soluble sulphate, which separated almost immediately, was collected and decomposed by aqueous sodium hydroxide, when the recovered base, after three crystallisations from benzene, melted at 238°. Harman was also prepared by O. Fischer's method from aminoharman and, as it was thought that the product might be contaminated with ethylharmol, it was boiled with an excess of concentrated hydriodic acid during an hour and the solution diluted, treated with sulphurous acid, and finally with an excess of sodium hydroxide. The precipitated base was collected, crystallised from benzene, and obtained in prisms melting at 238° alone or mixed with a specimen of harman pre-



pared as described above. The specimen of the base  $C_{12}H_{10}N_2$  which Professor Hopkins kindly sent us melted at  $238^\circ$  after two crystallisations and the melting point was not depressed by intimate mixture with an approximately equal amount of pure harman. Harman crystallises from benzene in well-defined prisms, the *sulphate*, from dilute sulphuric acid, in radiating clusters of short, delicate, microscopic needles and the *mercurichloride* from dilute hydrochloric acid containing mercuric chloride in long, slender needles. Under the microscope the latter are seen to extend across the field, and each crystal presents the appearance of two sharply defined, straight, parallel lines very close together. The respective crystalline forms and approximate solubilities of the base from tryptophan and its sulphate and mercurichloride were carefully compared with those of harman and the two salts thereof, with the result that complete identity was observed. O. Fischer states that solutions of salts of harman fluoresce blue, but we consider that it is violet, and the shade and intensity of fluorescence were identical in the cases of solutions of harman and of the base from tryptophan. The following experiments were carried out with both specimens and identical results observed. A trace of harman was boiled during five minutes with an excess of methyl iodide, after which the mixture was evaporated to dryness. The pale yellow residue which was sparingly soluble, even in boiling water, was heated with an aqueous suspension of freshly precipitated silver chloride and the solution filtered. The colourless aqueous solution of harman methochloride so obtained exhibited a bluish-violet fluorescence. On the addition of a drop of aqueous sodium hydroxide there was no precipitate, but, on the further addition of sodium hydroxide, a pale yellow precipitate was obtained. On shaking with benzene the latter extracted a bright yellow substance and the solution had a green fluorescence.

The benzene extract was separated and, on the addition of dilute hydrochloric acid, became colourless and the aqueous layer acquired a violet fluorescence. When harman is heated with phthalic anhydride a yellowish-brown fusion is obtained, and, on boiling with alcohol and cooling the solution, a sparingly soluble, orange, crystalline substance separates. The reaction is probably due to a condensation which involves the methyl group in the  $\alpha$ -position in the pyridine ring, and harmine exhibits a quite similar behaviour.

LXXXI.—*A New Photographic Phenomenon.*

By DONALD NEIL McARTHUR and ALFRED WALTER STEWART.

ALTHOUGH the phenomenon here described has not yet been entirely elucidated, the present preliminary note appears to be justified by the results which have already been obtained. A sensitive photographic plate is placed, film upward, at the bottom of a light-tight box; on the film are placed two or more glass microscope slides, and resting on these supports is laid a negative, also film side upward. The box is then closed and is placed in the neighbourhood of a Bunsen burner, a bat's-wing flame, or an electrical kettle-heater. After an exposure of some hours, the plate after development shows an image of the negative. The resulting photograph is the reverse of the original negative, that is, it is a positive such as would be obtained by simple printing with sensitised paper in the usual way.

In the experiments made, the plates used have been Wellington Anti-screen, Imperial Extra Rapid and Imperial Sovereign makes, different batches of each kind having been employed.

The material of the box may be either wood or cardboard. Care has been taken that no light enters the box; certain of the experiments having been conducted in total darkness, whilst in other cases the openings between the two halves of the boxes have been carefully sealed. The results are obtained whether the box is left in the open air or is enclosed in an air-tight desiccator.

The nature of the source of heat appears to exercise some influence on the rapidity with which the effects are produced. Very poor results are yielded by a Meker burner; poor results are given by a Bunsen flame impregnated with calcium salts; with lithium or sodium salts, the effects are more strongly marked. The electric heater gives very good results when worked on its lower resistance.

The distance between the box and the source of heat has usually been about 30—45 cm., but on one occasion results were obtained with a box placed in a cupboard 180 cm. away from a sodium burner, although in this case the exposure was an extremely prolonged one.

The most striking peculiarity of these experiments is the fact that when the box is arranged so that the sensitive plate lies between the source of heat and the negative, the results are obtained just as sharply as if the negative had been interposed between the heater and the sensitive plate. Were direct-acting rays concerned in the matter, it seems clear that in these circum-

stances the plate would be fogged by their passage through it before they reached the negative at all.

The results are not due to any radioactive material in the neighbourhood, for one of us carried out test experiments in the laboratory of the Queen's University of Belfast, where no radioactive contamination exists, and the effects were obtained there also.

The effects cannot be ascribed to the negative having stored up light which it liberates again in the dark, for a parallel experiment made with a negative which had been specially illuminated for ten minutes within 15 cm. of a spectroscopic spark apparatus gave no results when no source of heat was present.

The rays which produce the effects on the sensitive plate appear to be similar in properties to light rays. Glass is practically transparent to them; inkstains, seccotine, and metal show different degrees of opacity. It has been found that the rays can be diffracted and refracted just like ordinary light.

The matter is being further investigated, but the foregoing is sufficient to show that an interesting field has been opened up.

THE PHYSICAL CHEMISTRY LABORATORY,  
GLASGOW UNIVERSITY.

[Received, June 2nd, 1919.]

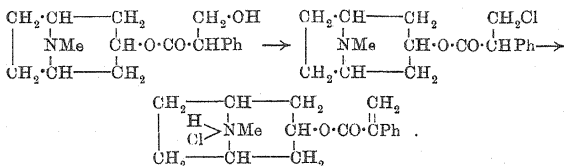
## LXXXII.—*The Stereochemistry of Hyoscine.*

By HAROLD KING.

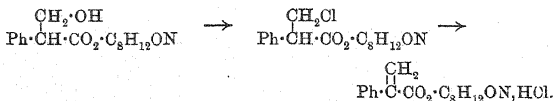
In a former communication (this vol., p. 476), it was shown that by resolution of a weakly active hyoscine by means of *d*- $\alpha$ -bromo- $\pi$ -camphorsulphonic acid, *d*-hyoscine bromocamphorsulphonate was obtained as the more sparingly soluble salt. The base proved to be the enantiomorph of the therapeutically valuable *l*-hyoscine of commerce. The unexpected discovery was made, however, that *d*- and *l*-hyoscines gave *dl*-oscine on hydrolysis with acid or alkali, whereas benzoyl-*d*-oscine under similar conditions gave optically pure *d*-oscine. Furthermore, the *d*- and *l*-oscine bases prepared by resolution of *dl*-oscine were not racemised by acid or alkali. On these grounds, *d*- and *l*-hyoscines were regarded as partially racemic esters, the optical activity being solely conditioned by the activity of the trotyl radicle.

In the present communication, further confirmatory evidence is adduced. In 1908, Wolfenstein and Mamlock (*Ber.*, **41**, 730) showed that atropine (trotyltropine) can be converted into

$\beta$ -chlorohydratropyltropine, and that, on evaporation of the ethereal solution of this base, an intramolecular change takes place, hydrogen chloride being transferred from carbon to nitrogen, with the formation of *apootropine* hydrochloride.



Willstätter and Hug (*Zeitsch. physiol. Chem.*, 1912, **79**, 146) showed that, in a precisely similar manner, *l*-hyoscyne on treatment with thionyl chloride gave  $\beta$ -chlorohydratropyloscine hydrochloride, and the ethereal solution of the base, on evaporation, gave *apohyoscyne* (*aposcopolamine*) hydrochloride.



This reaction destroys the asymmetry of the trotyl group, and could it be carried out under mild conditions, so as to preclude hydrolysis and racemisation, it should indicate whether the oscine portion of the molecule is active or inactive in *l*-hyoscyne. Willstätter and Hug, apparently unaware of the significance of this reaction, did not record the polarimetric examination of *apohyoscyne*. Moreover, they used potassium carbonate for liberating the bases from their salts, this alkali being known to racemise *l*-hyoscyne partly if contact is at all prolonged (Schmidt, *Arch. Pharm.*, 1898, **47**, 236), and their yield of *apohyoscyne* was only 50 per cent., the loss being attributed to hydrolysis. It has now been found that, on replacing potassium carbonate by the much weaker alkali sodium hydrogen carbonate, the reaction proceeds quantitatively throughout, and the resulting *apohyoscyne* is optically inactive.

To complete the proof of the partial racemic ester nature of *l*-hyoscyne, the resolution of *apohyoscyne* has been attempted.

*apoHyoscyne camphorsulphonate* (m. p. 157—158°) is a very readily soluble salt which can be recrystallised from a mixture of alcohol and ether, but shows no signs of resolution. The bromo-camphorsulphonate was not obtained crystalline, but the

*d*-hydrogen tartrate crystallises well from water. It contains two molecules of water of crystallisation, melts at 95—97°, and has  $[\alpha]_D + 8.6^\circ$  in water. Repeated crystallisation failed to change its melting point or its specific rotation.

The results so far obtained are best explained on the assumption already made that *d*- and *l*-hyoscines are partially racemic esters, *d*-hyoscine being composed of *d*-troyl-*d*-oscine and *d*-troyl-*l*-oscine, whilst *l*-hyoscine contains the enantiomorphs. Although *d*-hyoscine is not further resolved by *d*- $\alpha$ -bromo- $\pi$ -camphorsulphonic acid, it does not follow that *l*-hyoscine is not resolvable by the same acid or that either base is not resolvable by other optically active acids. The behaviour of pure *d*- and *l*-hyoscines towards the optically active acids, *d*-camphor- $\beta$ -sulphonic, *d*- $\alpha$ -bromo- $\pi$ -camphorsulphonic, and *d*-tartaric has now been investigated, but in no case was there any indication of resolution. The *d*-hydrogen tartrate of *d*-hyoscine could only be obtained as an uncrystallisable syrup.

The properties of the various crystalline camphorsulphonates are shown in the following table:

	<i>d</i> -Camphor- $\beta$ -sulphonate.			<i>d</i> - $\alpha$ -Bromo- $\pi$ -camphorsulphonate		
	M. p.	$[M]_D$ salt.	$[M]_D$ basic ion (calc.).	M. p.	$[M]_D$ salt.	$[M]_D$ basic ion (calc.).
<i>d</i> -Hyoscine	175—177°	+156.7°	+106.3°	158—160°	+370.5°	+91.8°
<i>l</i> -Hyoscine	186—187°	—40.8°	—91.2°	169—170°	+172.4°	—106.3°

The value obtained by direct observation on *d*- or *l*-hyoscine hydrobromides was  $[\alpha]_D \pm 33^\circ$  or  $[M]_D \pm 100^\circ$  (this vol., pp. 503, 504).

A peculiar numerical relationship is observable in the calculated molecular rotatory powers of the basic ions, the significance of which is not clear. It suggests a further resolution of *d*- and *l*-hyoscines, but, apart from these values, there is no evidence to support it, the picrate, for instance, prepared from *d*-hyoscine camphorsulphonate, being identical with that prepared from *d*-hyoscine bromocamphorsulphonate.

In addition to the above salts, *l*-hyoscine was found on one occasion to form a labile salt with *d*- $\alpha$ -bromo- $\pi$ -camphorsulphonic acid. This salt melted at about 150° and had  $[\alpha]_D + 25.5^\circ$ ,  $[M]_D + 157^\circ$ , but it was not obtained quite pure, as after two crystallisations it became transformed into the ordinary form of higher melting point (169—170°), and subsequent attempts to reproduce it were unsuccessful. Whether the tautomerism is centred in the bromocamphorsulphonic acid portion of the molecule, as has only rarely been observed (Kipping and Tattersall, T., 1903, 83, 918), or in the hyoscine portion of the molecule, must

for the present remain undecided. In this connexion, however, it is possibly significant that Wentzel (*Dissertation*, cited by Hesse, *J. pr. Chem.*, 1901, [ii], **64**, 274), by crystallising *l*-hyoscyne hydrobromide from alcohol, obtained a *laevo*-hyoscyne hydrobromide of much higher rotatory power, namely,  $[\alpha]_D -32.9^\circ$ , which fell, on keeping, to  $-25.8^\circ$ , the usually observed value. Hesse (*ibid.*, 353) claims to have partly substantiated this observation. This enhanced value for the anhydrous *l*-hyoscyne hydrobromide gives a calculated value  $[\alpha]_D +24.8^\circ$  for the *d*- $\alpha$ -bromo- $\pi$ -camphorsulphonate, a value of the same order as that observed,  $[\alpha]_D +25.5^\circ$ , for the labile bromocamphorsulphonate described above.

The present author has obtained another *l*-hyoscyne bromocamphorsulphonate,  $[\alpha]_D +17.9^\circ$ , m. p.  $200^\circ$ , during the resolution of a weakly active hyoscyne by means of  $\alpha$ -bromo- $\pi$ -camphorsulphonic acid. The amount of material was, however, only sufficient to prove the identity of the *l*-hyoscyne. It is not improbable that the acid contained in this salt is an isomeric acid which was present as an impurity in the original ammonium  $\alpha$ -bromo- $\pi$ -camphorsulphonate used.

#### EXPERIMENTAL.

##### *Preparation of dl-apoHyoscyne from l-Hyoscyne.*

The method employed for preparing this base is a modification of that given by Willstätter and Hug (*loc. cit.*).

*l*-Hyoscyne hydrobromide (3.87 grams) was converted into the base by the use of sodium hydrogen carbonate and chloroform. The chloroform-free base was warmed gently with 10 c.c. of thionyl chloride. The reaction proceeded smoothly, and, after keeping the product overnight, the thionyl chloride was distilled off under diminished pressure, and the last traces were removed by repeated extraction and evaporation with ether. The  $\beta$ -chlorohydratropyl-scine hydrochloride was dissolved in a little water, the solution rendered alkaline with sodium hydrogen carbonate, and the base thoroughly extracted with ether. Unlike *l*-hyoscyne, this chloro-substituted base could be readily extracted. The ethereal solution was evaporated to dryness, leaving a pale yellow oil, which immediately became opalescent, and, on digesting on the water-bath with fresh ether, no longer dissolved, but commenced to crystallise at the edges. On keeping for two days, it had crystallised completely in rosettes of stout needles consisting of *apohyoscyne* hydrochloride.

A 2.5 per cent. aqueous solution was neutral to litmus, and when examined in a 2-dcm. tube proved to have no action on the plane of polarised light.

The salt (2.7 grams) was dissolved in water (15 c.c.), the solution rendered alkaline with sodium hydrogen carbonate, and the base completely extracted with ether. On removal of the solvent, the base crystallised readily in rhomboidal plates. It melted at 75—78°, and amounted to 2.4 grams. Theory requires 2.5 grams. It was recrystallised from light petroleum (b. p. 40—60°), and separated in magnificent rhomboidal plates. The yield was 2.2 grams, and the base now melted at 79—80° (79—80° corr.).

The base was examined in 2.5 per cent. solution in absolute alcohol in a 2-dcm. tube, but was quite inactive.

Willstätter and Hug record the melting point 97° for *apo*hyoscine base, but this appears to be a misprint for 79°, as the nitrate, picrate, and aurichloride were found to melt at 157° (decomp.), 217—218°, and 188° respectively, in substantial agreement with Willstätter and Hug's recorded values, 157°, 217°, and 183—184° respectively. The appearance and solubilities of the base and these salts were also in agreement. (Aurichloride.—Found: Au=31.5.  $C_{17}H_{19}O_3N, AuCl_3, HCl$  requires Au=31.5 per cent.).

*dl-apoHyoscine Camphor-β-sulphonate.*

*apo*Hyoscine base was converted into its salt with camphor-β-sulphonic acid. It crystallised from a mixture of absolute alcohol and ether in irregular-shaped leaflets. It was recrystallised twice, yielding, finally, 0.65 gram melting at 157—158° (160.5—161.5° corr.).

The specific rotation was determined in water.

$c = 2.069$ ;  $l = 2$ -dcm.;  $\alpha + 0.404^\circ$ ;  $[\alpha]_D + 9.76^\circ$ ;  $[M]_D + 50.5^\circ$ .

The value of  $[M]_D$  is in excellent agreement with that recorded by Graham (T., 1912, 101, 747), namely,  $[M]_D + 50.4^\circ$  for the camphorsulphonic acid ion. That there was no resolution was confirmed by extracting the base from the solution, which had been used for determining the rotatory power, after rendering alkaline with sodium hydrogen carbonate and examining the solution of the base in absolute alcohol. It had no effect on the plane of polarised light.

The salt with *d*-α-bromo-π-camphorsulphonic acid was not obtained crystalline.

*dl-apoHyoscine d-Hydrogen Tartrate.*

One gram of *apo*hyoscine nitrate was regenerated to base, using sodium hydrogen carbonate and ether. The *d*-hydrogen tartrate

of the base was prepared in aqueous solution by combination with one equivalent proportion (0.45 gram) of *d*-tartaric acid. On concentrating the solution to about 10 c.c., *apohyoscine d*-hydrogen tartrate crystallised in clusters of radiating, white needles. The product was collected and washed with water. When dried in the air, it amounted to 1.15 grams. It was recrystallised four times from water, the properties of the successive fractions being as follows:

I. 1.15 grams,	m. p.	97°,	$[\alpha]_D + 8.74^\circ$ .
II. 1.0 gram,	,,	95—97°,	$[\alpha]_D + 8.35^\circ$ .
III. 0.75 ,,	,,	95—97°,	$[\alpha]_D + 7.78^\circ$ .
IV. 0.45 ,,	,,	95—97°,	$[\alpha]_D + 8.59^\circ$ .

Employing Landolt's value,  $[M]_D + 42.84^\circ$ , for ammonium hydrogen tartrate, the calculated value for *dl*-*apohyoscine d*-hydrogen tartrate is  $[\alpha]_D + 9.1^\circ$ , in approximate agreement with the values recorded above. The base when recovered from the fourth fraction was examined in absolute alcohol, but the solution was devoid of optical activity.

*dl*-*apohyoscine d*-hydrogen tartrate is sparingly soluble in cold, but dissolves freely in hot water. It crystallises with two molecular proportions of water in clusters of long needles. In a capillary tube it melts at 95—97° (95—97° corr.), and effervesces at 115°, but it melts below 90° when exposed on a watch-glass to a temperature of 90—95°. The water of crystallisation is not lost when the salt is dried in a vacuum over sulphuric acid:

0.1037, air-dried, gave 0.2031 CO<sub>2</sub> and 0.0579 H<sub>2</sub>O. C=53.4; H=6.2.

C<sub>17</sub>H<sub>19</sub>O<sub>3</sub>N, C<sub>4</sub>H<sub>6</sub>O<sub>6</sub>, 2H<sub>2</sub>O requires C=53.5; H=6.2 per cent.

The specific rotation was determined in dilute aqueous solution, using the air-dried salt.

$c = 2.008$ ;  $l = 2$ -dcm.;  $\alpha + 0.345^\circ$ ;  $[\alpha]_D + 8.6^\circ$ ;  $[M]_D + 40.5^\circ$ .

#### *d*-Hyoscine Camphor- $\beta$ -sulphonate.

Almost pure *d*-hyoscine base (1.5 grams) was neutralised with camphor- $\beta$ -sulphonic acid (1.15 grams). The syrupy salt was obtained crystalline by boiling with anhydrous ethyl acetate. It amounted to 2.3 grams and had  $[\alpha]_D + 27.6^\circ$ . It was recrystallised thrice more from anhydrous ethyl acetate, the specific rotation of the three fractions being successively  $[\alpha]_D + 29.5^\circ$ ,  $+ 29.4^\circ$ ,  $+ 29.3^\circ$ . The final fraction amounted to 1.5 grams.

*d*-Hyoscine camphor- $\beta$ -sulphonate crystallises well from anhydrous



ethyl acetate, in which it is sparingly soluble, in elongated, hexagonal-shaped leaflets or in acicular needles. Each fraction examined appeared to contain one molecule of water, which was lost at 95°. The anhydrous salt melted at 175—177° (179—181° corr.).

For the first crops of successive crystallisations, the percentage losses at 95° were 2.95, 3.33, 1.9, 2.95.

$C_{17}H_{21}O_4N, C_{10}H_{16}O_4S, H_2O$  requires  $H_2O = 3.25$  per cent.

0.1055, dried at 95°, gave 0.2339  $CO_2$  and 0.0663  $H_2O$ .  $C = 60.5$ ;  $H = 7.0$ .

$C_{17}H_{21}O_4N, C_{10}H_{16}O_4S$  requires  $C = 60.5$ ;  $H = 7.0$  per cent.

The specific rotatory power of the anhydrous salt was determined in water.

$c = 1.994$ ;  $l = 2$ -dcm.;  $\alpha + 1^\circ 10'$ ;  $[\alpha]_D + 29.25^\circ$ ;  $[M]_D + 156.7^\circ$ .

Employing the value  $[M]_D + 50.4^\circ$  for the camphor- $\beta$ -sulphonic acid ion, the calculated molecular rotation of the  $d$ -hyoscinium ion is  $[M]_D + 106.3^\circ$ , whence  $[\alpha]_D + 34.9^\circ$ . The value found by direct observation of  $d$ -hyoschine hydrobromide was  $[\alpha]_D + 33.2^\circ$  (this vol., p. 503).

The picrate prepared from the four times recrystallised camphor- $\beta$ -sulphonate by double decomposition was identical with  $d$ -hyoschine picrate obtained from  $d$ -hyoschine  $\alpha$ -bromo- $\pi$ -camphorsulphonate.

$d$ -Hyoschine  $d$ -hydrogen tartrate was prepared, but all attempts to crystallise it failed.

#### *l-Hyoschine Camphor- $\beta$ -sulphonate.*

Pure  $l$ -hyoschine base (1.4 grams) was neutralised in aqueous solution with Reychler's camphorsulphonic acid (1.0 gram). The dehydrated, syrupy salt was dissolved in anhydrous ethyl acetate, and, on keeping, crystallised homogeneously in clusters of large plates. The salt, when collected, amounted to 1.7 grams, melted at 187—188°, and had  $[\alpha]_D - 7.2^\circ$ . It was recrystallised twice more, the melting point remaining the same and the rotation being virtually unaltered with  $[\alpha]_D - 8.1^\circ$  and  $[\alpha]_D - 7.6^\circ$  successively.

*l-Hyoschine camphor- $\beta$ -sulphonate* crystallises from anhydrous ethyl acetate in transparent, rectangular plates. It melts at 186—187° (190—191° corr.):

0.2181, dried at 95°, lost nil.

0.0951 gave 0.2117  $CO_2$  and 0.0588  $H_2O$ .  $C = 60.7$ ;  $H = 6.9$ .

$C_{17}H_{21}O_4N, C_{10}H_{16}O_4S$  requires  $C = 60.5$ ;  $H = 7.0$  per cent.

The specific rotation was determined in water.

$c = 2.006$ ;  $l = 2$ -dcm.;  $\alpha - 18.33'$ ;  $[\alpha]_D - 7.6^\circ$ ;  $[M]_D - 40.8^\circ$ .

whence is calculated  $[M]_D$  for *l*-hyoscinium ion  $-91.2^\circ$  and  $[\alpha]_D - 30.0^\circ$ .

*l-Hyoscine d- $\alpha$ -Bromo- $\pi$ -camphorsulphonate.*

This salt crystallises from anhydrous ethyl acetate in minute needles. The rotation is unchanged after repeated crystallisation, 5.3 grams having  $[\alpha]_D + 28.28^\circ$  yielding, finally, 1.8 grams having  $[\alpha]_D + 28.05^\circ$ . It melts, when dried at  $110^\circ$ , at  $169-170^\circ$  ( $172.5-173.5^\circ$  corr.). It is deliquescent in a damp atmosphere, and then crystallises in microscopic, rectangular leaflets, probably a hydrated form. The anhydrous salt was analysed, with the following result:

0.2168, dried at  $95^\circ$ , lost 0.0003. Loss = 0.1 per cent.

0.0997, „ „  $95^\circ$ , gave 0.1934  $\text{CO}_2$  and 0.0538  $\text{H}_2\text{O}$ .

C = 52.9; H = 6.0.

$\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}, \text{C}_{10}\text{H}_{15}\text{O}_4\text{BrS}$  requires C = 52.7; H = 5.9 per cent.

The specific rotation was determined in water.

$c = 2.026$ ;  $l = 2\text{-dm.}$ ;  $\alpha + 1^\circ 8.2'$ ;  $[\alpha]_D + 28.05^\circ$ ;  $[M]_D + 172.4^\circ$ .

This gives a value  $[M]_D - 106.3^\circ$  for the molecular rotation of the *l*-hyoscinium ion and  $[\alpha]_D - 34.9^\circ$ .

*Labile Salt.*—On one occasion, a labile form of *l*-hyoscine bromocamphorsulphonate was isolated, the exact conditions being as follows. 7.5 Grams of freshly prepared, syrupy *l*-hyoscine bromocamphorsulphonate were repeatedly evaporated to dryness under diminished pressure with absolute alcohol in order to remove all adhering water. The residue, freed as completely as possible from absolute alcohol, was then dissolved in anhydrous ethyl acetate, and, on keeping for two days, a mixture of two salts separated in what appeared to be approximately equal proportions. One salt had the characteristic crystalline appearance of *l*-hyoscine *d*- $\alpha$ -bromo- $\pi$ -camphorsulphonate described above, but the other formed tufts of much larger needles with a more glistening appearance. A trace of each was removed, when the former melted at  $169-170^\circ$ , and was thus ordinary *l*-hyoscine bromocamphorsulphonate, whilst the second melted, either air-dried or dried at  $100^\circ$ , at  $150^\circ$ . The whole of the deposit was collected and recrystallised from ethyl acetate. It separated overnight in tufts of silky needles, which melted at  $150^\circ$ , but was contaminated by a much smaller proportion, this time, of ordinary *l*-hyoscine bromocamphorsulphonate, easily discernible as smaller, white tufts of needles. The product amounted to 3.6 grams.

$c = 2.068$ ;  $l = 2\text{-dm.}$ ;  $\alpha + 1^\circ 3.4'$ ;  $[\alpha]_D + 25.5^\circ$ .

This value is distinctly less than  $[\alpha]_D + 28.0^\circ$  observed for ordinary *l*-hyosine bromocamphorsulphonate. The product was again recrystallised, but gave the ordinary form of *l*-hyosine bromocamphorsulphonate melting at  $169-170^\circ$ . All attempts again to isolate this labile salt from this particular batch of material were unsuccessful.

*l*-Hyosine Bromocamphorsulphonate, m. p.  $200^\circ$ .

By resolution of a weakly active hyosine by *d*- $\alpha$ -bromo- $\pi$ -camphorsulphonic acid (this vol., p. 502), it was shown that the more sparingly soluble salt was *d*-hyosine  $\alpha$ -bromo- $\pi$ -camphorsulphonate, and that from the mother liquors a deliquescent salt having a specific rotation approximating to that of a *l*-hyosine *d*- $\alpha$ -bromo- $\pi$ -camphorsulphonate could be isolated.

The final mother liquor, on prolonged keeping at a low temperature, deposited 1.65 grams (1.6 per cent. yield) of a salt crystallising in rosettes of rectangular leaflets. It was not deliquescent and melted at  $199-200^\circ$  ( $203-204^\circ$  corr.).

The specific rotation was determined on material dried at  $95^\circ$ .

$c = 1.943$ ;  $l = 2$ -dm.;  $\alpha + 41.7'$ ;  $[\alpha]_D + 17.9^\circ$ .

0.1028 gram, dried at  $95^\circ$ , gave 0.1994  $\text{CO}_2$  and 0.0553  $\text{H}_2\text{O}$ .  
C = 52.9; H = 6.0.

$\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}, \text{C}_{10}\text{H}_{15}\text{O}_4\text{BrS}$  requires C = 52.7; H = 5.9 per cent.

0.1 Gram of this salt was converted into the picrate, which amounted to 0.09 gram and melted at  $183-186^\circ$ . On recrystallisation, it gave 0.08 gram melting at  $185-186^\circ$ , and when mixed with *l*-hyosine picrate, no depression in the melting point was observed.

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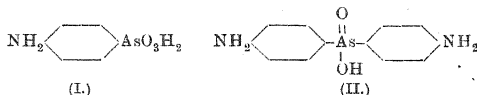
[Received, June 27th, 1919.]

### LXXXIII.—*Substituted Phenylarsinic Acids and their Reduction Products, and the Estimation of Arsenic in such Compounds.*

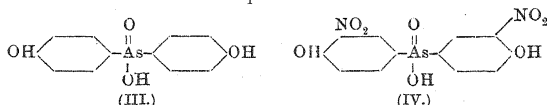
By ROBERT GEORGE FARGHER.

In the preparation of *p*-aminophenylarsinic acid (I) by Béchamp's method (*Compt. rend.*, 1863, 56, 1173), Pyman and Reynolds (T., 1908, 98, 1180) isolated as a by-product a small proportion of

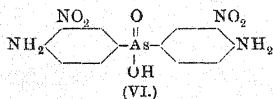
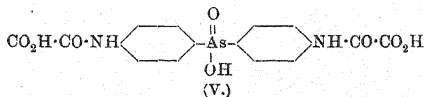
bis-*p*-aminophenylarsinic acid (*pp'*-diaminodiphenylarsinic acid) (II).



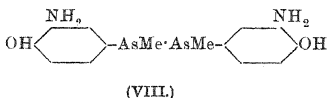
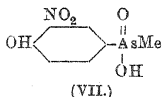
In view of the close relation existing between the two acids and the importance of the former as the starting point for the preparation of salvarsan, it seemed to be of interest to prepare the corresponding 3:3'-dinitro-4:4'-dihydroxydiphenylarsinic acid (IV) and to examine its reduction products.



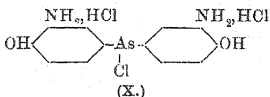
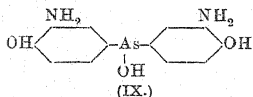
For the preparation of this acid, the two methods described for 3-nitro-4-hydroxyphenylarsinic acid (Bertheim, *Ber.*, 1911, **44**, 3092; Benda and Bertheim, *loc. cit.*, 3445; Benda, *loc. cit.*, 3449) can be used. In the first, the amino-acid (II) is converted into the corresponding hydroxy-acid (III) (Benda, *Ber.*, 1908, **41**, 2371) and subsequently nitrated under suitable conditions. This method gives excellent results. In the second, the amino-acid is converted into its *oxalyl* derivative (V), which is nitrated, the oxalyl group removed by acid hydrolysis, and the amino-group in the resulting 3:3'-dinitro-4:4'-diaminodiphenylarsinic acid (VI) subsequently replaced by hydroxyl by alkaline hydrolysis. The usefulness of this method is marred, however, by the fact that at temperatures approaching 140°, oxalic acid causes fission of the molecule of *pp'*-diaminodiphenylarsinic acid to some extent, the product being a mixture from which the *pp'*-dioxalylaminodiphenylarsinic acid can be isolated by means of the sparing solubility of its barium salt in cold dilute ammoniacal solution.



Bertheim (*Ber.*, 1915, **48**, 352), who described the preparation and reduction of 3-nitro-4-hydroxyphenylmethylarsinic acid (VII), found that the direct reduction of the nitro-acid with sodium hyposulphite led to an impure product, whilst if the hyposulphite reduction were stopped at the amino-acid stage and the reduction continued with hypophosphorous acid, 3:3'-diamino-4:4'-dihydroxydiphenyldimethyldiarsine (VIII) was obtained.

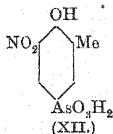
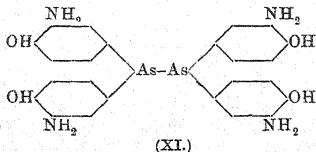


In the case of 3:3'-dinitro-4:4'-dihydroxydiphenylarsinic acid, complete reduction with sodium hyposulphite leads to 3:3'-diamino-4:4'-dihydroxydiphenylarsenious hydroxide (IX), for the crude, sparingly soluble reduction product, dissolved in methyl alcohol containing hydrochloric acid and precipitated with concentrated hydrochloric acid, gives rise to 3:3'-diamino-4:4'-dihydroxydiphenylarsenious chloride dihydrochloride (X), which was obtained in a crystalline condition.



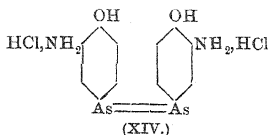
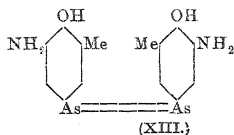
If the acid is first reduced to the corresponding *amino-acid* by means of sodium hyposulphite and then completely reduced by means of hypophosphorous acid, 3:3':3'':3'''-tetra-amino-4:4':4'':4'''-tetrahydroxytetraphenyldiarsine (XI) is obtained.

The degree of reduction of the products is readily ascertained by titration with a standard solution of iodine, using starch as indicator, oxidation to the corresponding arsenic acids taking place (compare Gaebel, *Arch. Pharm.*, 1911, **249**, 241).

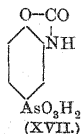
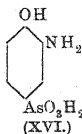
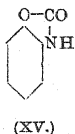


5-Nitro-6-hydroxy-*m*-tolylarsinic acid (XII), first obtained by Benda and Bertheim (*loc. cit.*) by the nitration of 4-hydroxy-*m*-

tolylarsinic acid, can also be prepared from 4-oxalylamino-*m*-tolyl-*arsinic acid* by the series of reactions outlined above, the preparations from both sources being identical. On reduction with sodium hyposulphite, diaminoarseno-*o*-cresol (4:4'-dihydroxy-5:5'-diamino-3:3'-dimethylarsenobenzene) (XIII) (D.R.-P. 224953) was obtained. This was converted into the *dihydrochloride*, which closely resembles salvarsan (XIV).



By the action of carbonyl chloride on *o*-aminophenol, 1:2-dihydrobenzoxazolone (XV) is obtained (Schmitt and Henschel, *J. pr. Chem.*, 1888, [ii], 37, 27; E. von Meyer, *ibid.*, 1915, [ii], 92, 255). This reaction was applied to 3-amino-4-hydroxyphenylarsinic acid (XVI), giving 1:2-dihydrobenzoxazolone-4-arsinic acid (XVII), which, on reduction with sodium hyposulphite, yielded the corresponding *arsenobenzene*. It had been hoped that this would prove sufficiently acidic to dissolve in sodium carbonate, but although it dissolves very readily in sodium hydroxide, it is practically insoluble in the carbonate.



The estimation of arsenic in organic compounds has been the subject of a recent communication by Ewins (T., 1916, 109, 1355), who considers that the method devised by Lehmann (*Apoth. Zeit.*, 1912, 27, 545) for the estimation of arsenic in salvarsan and neo-salvarsan, whilst applicable to certain closely allied derivatives, fails entirely in a large number of cases owing to the fact that the preliminary treatment with potassium permanganate and sulphuric acid does not bring about complete oxidation. By a slight alteration of the conditions, it has now been found possible to extend this estimation to a considerable number of substituted phenyl-arsinic acids containing nitro-, amino-, hydroxy-, methoxy-, bromo-, and other groups, which, by the unmodified method, gave very untrustworthy results owing to incomplete oxidation.

## EXPERIMENTAL.

*pp'*-Dihydroxydiphenylarsinic Acid (III).

*pp'*-Dihydroxydiphenylarsinic acid was obtained by Benda (*Ber.*, 1908, **41**, 2371) by diazotising *pp'*-diaminodiphenylarsinic acid in dilute hydrochloric or sulphuric acid, and decomposing the diazo-derivative by passing steam through the solution. Diazotisation in hydrochloric acid, however, gives a product substituted to some extent by chlorine, whilst in sulphuric acid alone the product is very dark-coloured and difficult to purify.

10.5 Grams of sodium *pp'*-diaminodiphenylarsinate, containing  $6\text{H}_2\text{O}$ , were dissolved in 75 c.c. of water, 10 c.c. of sulphuric acid added, and diazotised with 50 c.c. of a normal solution of sodium nitrite. The product was mixed with an equal volume of acetic acid to keep the hydroxy-acid produced in solution, and warmed on the water-bath until the elimination of nitrogen had ceased. After boiling with charcoal, the solution was concentrated under diminished pressure, when, on cooling, rather more than 5 grams of the hydroxy-acid separated, whilst the mother liquors yielded further small quantities, the total yield amounting to 75–80 per cent. of the theoretical. The acid is very sparingly soluble in acetone or chloroform, but readily so in methyl alcohol, ethyl alcohol, or 50 per cent. acetic acid, from which it crystallises in plates melting and decomposing at  $259^\circ$  (corr.). (Found: C=49.0; H=3.7; As=25.3.  $\text{C}_{12}\text{H}_{11}\text{O}_4\text{As}$  requires C=49.0; H=3.8; As=25.5 per cent.)

*3:3'-Dinitro-4:4'-dihydroxydiphenylarsinic Acid (IV).*

6.3 Grams of *pp'*-dihydroxydiphenylarsinic acid were dissolved in 35 c.c. of concentrated sulphuric acid and treated gradually with a mixture of 2.5 c.c. of nitric acid (D 1.44) and 2.5 c.c. of sulphuric acid, the temperature being kept at  $-5^\circ$  to  $-3^\circ$ . After the mixture had remained in a cool place for some time, it was poured on 250 grams of powdered ice, the precipitated acid being collected and washed with water. The yield amounted to 94 per cent. of the theoretical. The acid is almost insoluble in boiling water, fairly readily soluble in glacial acetic acid, and sparingly so in 50 per cent. acetic acid, from which it separates in minute, rhomboidal prisms melting and decomposing at  $230^\circ$  (corr.).

Found: C=37.5; H=2.6; N=7.3; As=19.6.

$\text{C}_{12}\text{H}_9\text{O}_8\text{N}_2\text{As}$  (384.1) requires C=37.5; H=2.4; N=7.3; As=19.5 per cent.

*3:3'-Diamino-4:4'-dihydroxydiphenylarsenious Chloride  
Dihydrochloride (X).*

Two grams of the preceding compound, dissolved in 20 c.c. of water and 5.4 c.c. of 2*N*-sodium hydroxide, were added to a solution of 6 grams of magnesium chloride and 24 grams of sodium hyposulphite in 200 c.c. of water. The resulting solution, which immediately decolorised, was heated to 60° in an atmosphere of carbon dioxide for an hour, a further 10 grams of sodium hyposulphite being added after half an hour. The small quantity of grey powder obtained was dissolved in a little methyl alcohol containing hydrochloric acid, filtered, and added to 100 c.c. of concentrated hydrochloric acid, when a crystalline precipitate gradually separated. This was collected, washed with a few drops of glacial acetic acid and a little ether, and dried in a vacuum over sulphuric acid, the yield amounting to 0.5 gram.

The compound forms glistening leaflets readily soluble in water or methyl alcohol, but sparingly so in concentrated hydrochloric acid. On heating, it darkens above 170° and melts at 215° (corr.).

Found: C=36.2; H=3.8; N=6.9; Cl=27.0.

$C_{12}H_{12}O_2N_2ClAs \cdot 2HCl$  (399.5) requires C=36.0; H=3.5; N=7.0; Cl=26.7 per cent.

0.1000 Gram required 0.061 gram of iodine for complete oxidation, against 0.063 theoretically required.

*3:3'-Diamino-4:4'-dihydroxydiphenylarsinic Acid and  
3:3':3'':3'''-Tetra-amino-4:4':4'':4'''-tetrahydroxytetra-  
phenyldiarsine Tetrahydrochloride.*

5.1 Grams of 3:3'-dinitro-4:4'-dihydroxydiphenylarsinic acid were dissolved in 80 c.c. of water and 24 c.c. of 2*N*-sodium hydroxide. The solution, cooled to 0°, was treated in one operation with 17.6 grams of commercial sodium hyposulphite, the temperature rising to about 30°. When the reaction was complete, the solution was cooled, 20 c.c. of 2*N*-hydrochloric acid were added, and as the acid only partly separated, it was salted out by the addition of sodium chloride, and was obtained as a sandy, crystalline precipitate fairly readily soluble in water or methyl alcohol, but sparingly so in ethyl acetate. The yield amounted to 46 per cent. of the theoretical. (Found: N=8.5.  $C_{12}H_{13}O_4N_2As$  (324.1) requires N=8.6 per cent.)

Two grams of the acid were heated at 60° for one hour in an atmosphere of carbon dioxide with 20 c.c. of hypophosphorous acid



(D 1.15) and a trace of hydriodic acid. As the colourless base obtained by neutralising a test portion of the resulting solution rapidly became purple on exposure, the remainder was added without neutralisation to 150 c.c. of hydrochloric acid. The white precipitate which gradually separated was collected, washed with a few drops of glacial acetic acid and a little dry ether, and dried in a vacuum. The product is readily soluble in water or methyl alcohol.

Found: N=7.6; Cl=19.7.

$C_{24}H_{24}O_4N_4As_2 \cdot 4HCl$  (728.1) requires N=7.7; Cl=19.5 per cent.

0.1001 Gram required 0.103 gram of iodine for complete oxidation, as against 0.104 gram theoretically required.

#### *pp'*-Dioxalylaminodiphenylarsinic Acid (V).

When oxalic acid is allowed to react with *pp'*-diaminodiphenylarsinic acid at a temperature approaching  $160^\circ$ , some fission of the molecule results, so that a mixture is obtained from which the desired product can be isolated by taking advantage of the sparing solubility of its barium salt in cold dilute ammonia, the barium salt of *p*-aminophenylarsinic acid being precipitated only on boiling.

8.4 Grams of sodium *pp'*-diaminodiphenylarsinate containing  $6H_2O$  were intimately mixed with 15.1 grams of oxalic acid and heated in an oil-bath with constant stirring at  $140^\circ$  until most of the water had disappeared, and then to  $160^\circ$  until quite hard. The product was well ground with 80 c.c. of water and 8 c.c. of hydrochloric acid, collected, and well washed with water. It was then dissolved in ammonia and treated with a cold solution of barium chloride. The resulting precipitate was collected, well washed with water, and decomposed by grinding with dilute hydrochloric acid. A small quantity which remained in the acid was precipitated on dilution. *pp'*-Dioxalylaminodiphenylarsinic acid is only sparingly soluble in boiling water, alcohol, or methyl alcohol, and practically insoluble in benzene, ether, or ethyl acetate. It is more readily soluble in acetic acid or 50 per cent. acetic acid, and crystallises in slender needles which contain  $4H_2O$ .

Found: loss at  $110^\circ$ =13.8.

$C_{16}H_{13}O_8N_2As \cdot 4H_2O$  requires 14.1 per cent.

In material dried at  $110^\circ$ , C=44.1; H=3.3; N=6.4.

$C_{16}H_{13}O_8N_2As$  (436.2) requires C=44.0; H=3.0; N=6.4 per cent.

Nitration with a mixture of nitric and sulphuric acids, and subsequent acid hydrolysis, led to the formation of 3:3'-dinitro-4:4'-

*diaminodiphenylarsinic acid* (VI), a yellow, crystalline powder very sparingly soluble in water and the usual organic solvents.

Found: N=14.3.

$C_{12}H_{11}O_6N_4As$  (382.1) requires N=14.7 per cent.

This was converted by warming with an excess of potassium hydroxide solution into 3:3'-dinitro-4:4'-dihydroxydiphenylarsinic acid, identical with that described above.

#### *6-Oxalylamino-m-tolylarsinic Acid.*

Five grams of sodium 6-amino-*m*-tolylarsinate (containing  $3H_2O$ ) and 6 grams of oxalic acid were intimately mixed and heated first at  $140^\circ$  until most of the water had been driven off, and then at  $160^\circ$  until quite dry. The residue was triturated with 50 c.c. of water and 7 c.c. of hydrochloric acid, collected, and washed with water. The product, which was anhydrous, amounted to rather more than 3 grams. It was found to be sparingly soluble in hot alcohol, ethyl acetate, or acetone, more readily so in hot water, and readily so in 50 per cent. acetic acid, from which it crystallised in elongated, rhombic prisms.

Found: N=4.5; As=24.6.

$C_9H_{10}O_6NAs$  (303.1) requires N=4.6; As=24.7 per cent.

#### *5-Nitro-6-amino-m-tolylarsinic Acid.*

Six grams of the above oxalyl derivative were dissolved in 20 c.c. of sulphuric acid, and a mixture of 1.2 c.c. of nitric acid (D 1.4) and 1.2 c.c. of sulphuric acid was gradually added below  $15^\circ$ . When the reaction was complete, the product was poured into 100 c.c. of water, boiled under a reflux condenser for two hours, cooled, and the acid which separated, amounting to 4.6 grams, collected. *5-Nitro-6-amino-m-tolylarsinic acid* is fairly readily soluble in boiling water, from which it separates in slender needles consisting of a mixture of the yellow anhydrous form and the orange hydrated form. It gradually passes completely into the latter, which contains  $1\frac{1}{2}H_2O$ .

Found: loss at  $110^\circ=9.3$ .

$C_7H_9O_5N_2As, 1\frac{1}{2}H_2O$  requires  $H_2O=9.0$  per cent.

In dried substance, N=9.9.

$C_7H_9O_5N_2As$  (276.1) requires N=10.1 per cent.

*5-Nitro-6-hydroxy-m-tolylarsinic Acid (XII).*

Two grams of the acid just described were heated on the water-bath with 10 c.c. of 40 per cent. potassium hydroxide solution until a test portion no longer showed the presence of an amino-group. The product was then cooled and acidified with hydrochloric acid, giving almost the theoretical yield of 5-nitro-6-hydroxy-*m*-tolylarsinic acid. This was compared with a specimen prepared by Benda and Bertheim's method (*Ber.*, 1911, **44**, 3445), and found to be identical with it. Both products, when crystallised rapidly from boiling water, formed clusters of slender, yellow needles, and when crystallised slowly from 50 per cent. acetic acid, well-defined, rhombic prisms. When heated in the same bath, both products decomposed explosively at 310°, whilst the mixture of the two behaved identically.

The *acetyl* derivative, prepared by the action of acetic anhydride in the presence of a trace of pyridine, is fairly readily soluble in methyl or ethyl alcohol or boiling water, but sparingly so in cold water or ethyl acetate. When crystallised from water, it forms colourless, spherical nodules, which are anhydrous.

Found: N=4.4.

$C_9H_{10}O_7Na_3$  (319.1) requires N=4.4 per cent.

*4:4'-Dihydroxy-5:5'-diamino-3:3'-dimethylarsenobenzene Dihydrochloride.*

The reduction of the 5-nitro-6-hydroxy-*m*-tolylarsinic acid was effected by means of sodium hyposulphite under the conditions described by Ehrlich and Bertheim (*Ber.*, 1912, **45**, 757; compare D.R.-P. 224953). The dihydrochloride, which was obtained in a yield of 70 per cent. of the theoretical, formed a pale yellow, micro-crystalline powder readily soluble in water or methyl alcohol, much less readily so in ethyl alcohol, and practically insoluble in ether or acetone.

Found: Cl=13.6; As=29.9.

$C_{14}H_{16}O_2N_2As_2 \cdot 2HCl \cdot 2H_2O$  (503.1) requires Cl=14.1; As=29.8 per cent.

*3-Amino-4-hydroxyphenylarsinic Acid.*

The reduction of nitrohydroxyphenylarsinic acid to the corresponding amino-acid by means of sodium hyposulphite has been

described in D.R.-P. 224953. The following modification of the method gives excellent results.

Twenty-six grams of 3-nitro-4-hydroxyphenylarsinic acid were dissolved in 200 c.c. of *N*-sodium hydroxide, cooled to  $-2^{\circ}$ , and to the well-stirred solution 65 grams of sodium hyposulphite (80 per cent.) were added in one operation. The colour of the solution disappeared at once, and the temperature rose to  $25^{\circ}$ , whilst the amino-acid commenced to deposit. The precipitation was completed by the addition of 23 c.c. of hydrochloric acid (D 1.12). The acid was collected and well washed with water; the yield in several experiments ranged between 65 and 80 per cent. of the theoretical.

*1:2-Dihydrobenzoxazolone-4-arsinic Acid (XVII).*

A solution of 11.6 grams of aminohydroxyphenylarsinic acid in 150 c.c. of 5 per cent. sodium hydroxide, cooled by ice and stirred vigorously, was gradually treated with 110 c.c. of a 6.5 per cent. solution of carbonyl chloride in toluene. At the conclusion of the reaction, the two layers were separated, the aqueous layer being extracted with ether and then acidified with hydrochloric acid, when the oxazolone separated as a sandy, crystalline precipitate in a yield amounting to 83 per cent. of the theoretical.

It is sparingly soluble in alcohol, but readily so in boiling water, from which it separates in colourless, prismatic needles which are anhydrous. On heating, it rapidly decomposes above  $250^{\circ}$  without melting.

Found: C=32.5; H=2.5; N=5.4; As=28.6.

$C_7H_6O_5NaAs$  (259.0) requires C=32.4; H=2.3; N=5.4; As=28.9 per cent.

*1:2:1':2'-Tetrahydro-4-arsenobenzodioxazolone.*

2.3 Grams of 1:2-dihydrobenzoxazolone-4-arsinic acid were dissolved in a mixture of 50 c.c. of water and 8 c.c. of 2*N*-sodium hydroxide, added to a solution of 15 grams of sodium hyposulphite and 3 grams of magnesium chloride in 70 c.c. of water, and heated, with stirring, for an hour at  $60^{\circ}$  in an atmosphere of carbon dioxide. A yellow, granular precipitate gradually formed, which, after cooling, was collected and well washed with water. A portion was dried to constant weight in a vacuum over sulphuric acid, and formed a pale yellow, granular powder insoluble in water or the usual organic solvents or in sodium carbonate, but readily soluble in aqueous sodium hydroxide.

Found: N=6.5; As=35.6.

$C_{14}H_9O_4N_2As_2$  (418.1) requires N=6.7; As=35.9 per cent.

The remainder was dissolved in aqueous sodium hydroxide, and the sodium salt precipitated by the addition of alcohol. This, after drying in a vacuum, was obtained as a pale yellow, fairly stable powder readily soluble in water, sparingly so in alcohol, and insoluble in ether.

*Estimation of Arsenic in Substituted Phenylarsinic Acids.*

For the estimation of arsenic in the foregoing and many other compounds, the following modification of Lehmann's method (*Apoth. Zeit.*, 1912, 27, 545) has been used, and has been found to give good results generally with substituted phenylarsinic acids.

0.2 Gram of the powdered substance is accurately weighed and intimately mixed in a 250 c.c. flask with 1 gram of potassium permanganate. Five c.c. of 50 per cent. sulphuric acid are added, followed by a further 10 c.c. of concentrated sulphuric acid when the first reaction has ended. After a few minutes, 10 c.c. of water are added, and the mixture is heated for half an hour to gentle boiling, precautions being taken against loss by spraying. The manganese dioxide is then removed by a slight excess of hydrogen peroxide, 30 c.c. of water are added, and the solution is again boiled for ten minutes, after which a dilute solution of potassium permanganate is added drop by drop until a faint, permanent pink tinge is obtained. This is discharged by the addition of a drop of a dilute solution of oxalic acid. The solution is then cooled, 2.5 grams of potassium iodide are added, the whole being allowed to remain for an hour, and the liberated iodine titrated by means of thiosulphate. A blank experiment should be carried out alongside each estimation, and the final reading corrected accordingly.

The following are examples of the results obtained:

Substance.	As	
	Found.	Calc.
3-Nitro-4-hydroxyphenylarsinic acid.....	28.4, 28.4	28.5
p-Aminophenylarsinic acid .....	34.5, 34.5	34.6
1:2-Dihydrobenzoxazolone-4-arsinic acid .....	28.6	28.9
3-Nitro-4-aminophenylarsinic acid.....	28.9, 28.8	28.6
3:3'-Dinitro-4:4'-dihydroxydiphenylarsinic acid.....	19.6, 19.5	19.5
p-Bromophenylarsinic acid .....	26.5	26.7

In conclusion, the author desires to express his thanks to Professor F. L. Pyman for his interest during the course of the investigation.

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### LXXXIV.—*The Selective Combustion of Carbon Monoxide in Hydrogen.*

By ERIC KEIGHTLEY RIDEAL.

In a recent communication (*Analyst*, 1919, **44**, 89), it was shown that small quantities of carbon monoxide in hydrogen could be preferentially oxidised to carbon dioxide by passing the gaseous mixture admixed with a small quantity of oxygen over certain catalytic materials maintained at suitable temperatures.

The following conclusions were drawn, namely, that the preferential nature of the combustion was affected by the nature and temperature of the catalyst employed; thus, the oxides of copper (operative at 110°) and of iron and chromium (operative at 250° to 350°) were extremely efficacious in inducing the combustion of the carbon monoxide, whilst an enhanced activity could be obtained by the addition of certain promoters, such as ceria and thoria, in small quantities to the mixed oxides. With reduced nickel, on the other hand, complete interaction of oxygen and the hydrogen was obtained. At the time, it was considered probable that with suitable catalytic material maintained at the proper temperatures only carbon monoxide, and no hydrogen, could be burnt, the selective nature of the reaction being gradually lost with elevation of the temperature. It was also established that complete elimination of the carbon monoxide could be effected by this means, and that the mechanism was not founded on the operation of the water-gas reaction,  $\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{H}_2 + \text{CO}_2$ , at low temperatures.

In view of the importance of the processes of selective combustion, such as of hydrogen sulphide in hydrogen, phosphine in ammonia, which are being investigated, and of the present example, it was deemed of interest to study the mechanism of the reaction in somewhat greater detail in order, if possible, to obtain material to assist in making a decision as to the validity of the various theories of heterogeneous catalysis which are now extant. In the case of the catalytic combination of hydrogen and oxygen on the surface of platinum black, the theory of an intermediate compound is strongly supported by the work of Engler and Wöhler (*Zeitsch. anorg. Chem.*, 1901, **29**, 1; *Ber.*, 1903, **36**, 2642), whilst Sabatier, in his researches on hydrogenation by means of metallic nickel, concluded that his results were explicable on the assumption that an unstable nickel hydride was formed ("La Catalyse en Chimie Organique").

Faraday (*Phil. Trans.*, 1834, **114**, 55), on the other hand, gave ardent support to the adsorption theory. Recently, Bancroft (*J. Physical Chem.*, 1917, **21**, 8), from a survey of the work of Turner, Henry, Luuge, Harbeck, and Bone, draws the conclusion that the facts are capable of the simplest explanation on the adsorption theory.

The adsorption theory, however, is capable of several interpretations, which at the present time are developing along two distinct lines, that may be termed the *diffusion theory* and the *single layer theory*. In the diffusion theory, which finds its expression in the work of Bodenstein (*Zeitsch. physikal. Chem.*, 1899, **29**, 655, *et seq.*), and for which some support can be gained from the experiments of Bone and his co-workers (*Phil. Trans.*, 1906, [A], **206**, 1), the adsorbed layer is relatively thick and the velocity of reaction is governed rather by the rate of diffusion of the reactants and products in this layer than by the rate of chemical change occurring at the actual surface of the catalyst. In the single layer theory, advanced by Langmuir (*J. Amer. Chem. Soc.*, 1916, **38**, 2221; 1917, **39**, 1848; 1918, **40**, 1361), Harkins (*ibid.*, 1917, **39**, 591), and Marcelin, the surface film is considered to be only one molecule thick, thus showing an abrupt change in continuity, and the reactions take place in that surface skin. Lewis (this vol., p. 182) has recently applied the radiation hypothesis to explain the enhanced reaction velocities obtained in the presence of heterogeneous catalytic materials, and has adopted the "single layer" theory as "the most probable material mechanism of the process considered." A summary of the results of Bodenstein and Bone and Wheeler on the catalytic combination of hydrogen and oxygen is likewise given in this paper. Bodenstein and Ohmer's investigations (*Zeitsch. physikal. Chem.*, 1905, **53**, 166) on the catalytic combination of carbon monoxide and oxygen on the surface of hot quartz between 300° and 570° led them to the conclusion that the rate of combination was proportional to the partial pressure of the oxygen and inversely proportional to the concentration of carbon monoxide, a case of negative catalysis; estimations were carried out by the manometric method.

#### EXPERIMENTAL.

The catalytic materials investigated were prepared as follows:

*Iron oxide*, prepared by the gentle ignition of the nitrate, the remainder of the oxides of nitrogen being expelled by heating in a current of steam at 400°. The coarse lumps obtained in this way were broken up, and uniform pieces, some 0.2 cm. in diameter, utilised for experimental purposes.

*Iron oxide* containing 2·5 per cent. of chromium oxide and 0·5 per cent. of cerium oxide, prepared in a similar manner from the nitrates of iron and cerium with the admixture of the chromium salt in the form of ammonium dichromate.

*Copper oxide* prepared from copper wire by alternate oxidation and reduction with air and hydrogen respectively. The gases were carefully freed from any possible contamination with hydrogen sulphide or sulphur dioxide. The copper oxide was considered sufficiently active when appreciable quantities of water were formed when hydrogen was passed over it at 120°.

*Nickel* prepared by soaking small pieces of diatomite in nickel nitrate, followed by gentle ignition and heating in superheated steam. The finished product contained 5 per cent. of nickel.

*Palladium*.—An ordinary purchased sample of good quality palladised asbestos was used for this purpose.

Preliminary experiments having shown that it was extremely difficult to prepare two specimens of catalytic material identical in activity, and, further, that the activity of the catalyst underwent marked fluctuations in the course of an experiment, first increasing and then decreasing, it was decided not to attempt to measure the relative velocities of catalytic combustion of hydrogen and carbon monoxide in separate experiments, but to determine the relative rates of combustion of these constituents in gas mixtures containing hydrogen, oxygen, and carbon monoxide.

The gas mixtures of various compositions were obtained from electrolytic hydrogen and oxygen and carbon monoxide produced from oxalic and sulphuric acids, the carbon dioxide being removed by means of sodium hydroxide. Prior to use, the gas mixture was carefully freed from any traces of carbon dioxide and from moisture by means of soda-lime and phosphoric oxide.

The furnace was similar to that employed in the analytical instrument previously mentioned, but was constructed throughout of silica instead of glass. It consisted essentially of two co-axial silica tubes, the outer one electrically heated and so arranged that the gases could pass in through the annular space between the tubes and down through the catalyst in the central tube. In this way, uniformity of temperature in the catalyst was ensured.

In each experiment, 5 c.c. of catalyst were employed; no attempt was made to approximate to the same superficial area of catalytic material, although experiments have shown that with a uniform catalytic material the activity is proportional to the superficial area of the grains; this generalisation, however, does not apply to fine powders or to relatively large pieces of porous materials.

A series of experiments was conducted by passing the gas mixture through the catalytic material maintained at suitable tempera-



tures, and determining the quantities of water and carbon dioxide formed by the usual methods adopted in processes of organic combustion, namely, absorption and weighing. In all cases, the temperature was accurately controlled by means of a thermometer, around the bulb of which the catalytic material was built up, and care was taken to ensure passage of the gas mixture through the furnace at such a rate that the fractional conversion was but small. This consideration is of some importance in the light of the diffusion theory, for if we imagine the surface of the catalyst to be covered with a small atmosphere of the products of the reaction, carbon dioxide and steam, then, if the gas is quiescent, fresh reactants can only approach the catalyst by diffusion, and the atmosphere will slowly extend from the surface of the catalyst to the walls of the containing vessel. Under these conditions, the phenomenon of catalysis is not being observed, but there are recorded merely some rates of diffusion liable to large errors caused by convection, especially if the reaction is strongly exothermic. A gentle movement of the gas will consequently upset these conditions, and the rates of reaction will be affected by the nature and magnitude of this movement.

This does not necessarily preclude the diffusion theory of catalysis, since in this case it is assumed that the atmosphere round the catalyst is maintained by the molecular forces of the material, and that the "diffusion layer," as in the case of liquid and solid surfaces investigated by Noyes and Whitney (*Zeitsch. physikal. Chem.*, 1897, **23**, 689), is relatively thin—of the order of 0.05 to 0.1 mm. It will therefore suffice always to maintain the gas velocity past the catalyst grains, so that the "diffusion layer," if it exists at all, will not exceed the normal thickness produced by adsorption. On the other hand, the velocity of the flow of gas must not be raised too high, since evidence is not lacking in the possibly analogous case of liquid and solid surfaces that the adsorption film is affected by high velocities; thus, A. Fischer and the author computed that the thickness of the film was reduced from 0.0635 mm. to 0.0510 mm. by agitating the liquid by means of a stirrer rotating at 250 and 1100 revolutions per minute respectively.

In the first series of experiments, a mixture containing approximately 10 per cent. of carbon monoxide, 10 per cent. of oxygen, and 80 per cent. of hydrogen was passed through the various catalytic materials at various temperatures from 150° to 380°. Below 150°, the activity of all the catalysts employed, with the exception of palladium, was too slight to yield trustworthy results, and at high temperatures the activity became so great that, in spite of reducing

the quantity of catalyst in the furnace and considerably augmenting the velocity of the gas, a very considerable conversion of the reactants took place, which, for the reasons already stated, was undesirable.

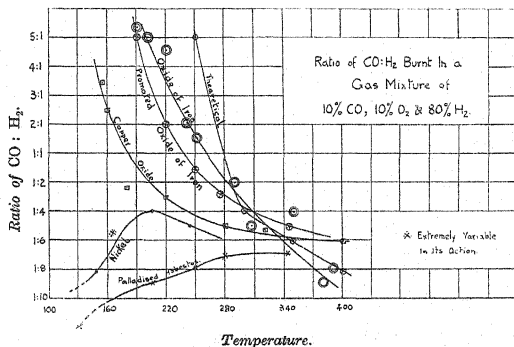
The results of these experiments are shown in the attached curves, from which the two following typical examples may be cited:

Catalyst, iron oxide.

Temperature, 220°.

Composition of gas: CO=9; O<sub>2</sub>=14; H<sub>2</sub>=77 per cent.

Vol. of gas used. Litres.	Time in hours.	Weight of H <sub>2</sub> O collected.	Weight of CO <sub>2</sub> collected.	Ratio vol. CO : H <sub>2</sub> burnt.
0.768	1.5	0.0121	0.1332	4.43 : 1
0.568	1.75	0.0092	0.0964	4.22 : 1
0.424	2.0	0.0062	0.0702	4.28 : 1
Mean.....				4.32 : 1



Catalyst, copper oxide.

Temperature, 280°.

Composition of gas: CO=14; O<sub>2</sub>=11.5; H<sub>2</sub>=74.5 per cent.

Vol. of gas used. Litres.	Time in hours.	Weight of H <sub>2</sub> O collected.	Weight of CO <sub>2</sub> collected.	Ratio vol. CO : H <sub>2</sub> burnt.
1	0.5	0.0442	0.0503	0.470 : 1
1	0.5	0.0298	0.0344	0.472 : 1
1	0.5	0.0390	0.0431	0.452 : 1
Mean.....				0.466 : 1

In all cases, the interesting observation was made that a catalyst which had been allowed to cool exposed to the air, liberated first, on warming in the stream of gas, a relatively large quantity of carbon dioxide, and, at higher temperatures, water vapour; further, on raising the temperature of a catalyst in the mixture of gases, the ratio  $\text{CO}:\text{H}_2$  burnt, as obtained by estimation of the water and carbon dioxide, during the first twenty minutes or so, fell short of the ratio when constant velocity ratios were obtained.

In the second series of experiments, only one catalytic material was employed, namely, iron oxide, and the gaseous mixture was altered in composition in order to determine the effect of an alteration in the partial pressures of the reactants on the relative rates of reaction.

In these experiments, the temperature of the catalyst was maintained at  $220^\circ$ , when the following ratios were obtained:

Expt. No.	Composition of gas per cent.			Ratio $\text{CO}:\text{H}_2$ by volume burnt.
	CO.	$\text{O}_2$ .	$\text{H}_2$	Mean of several experiments.
1	12.3	10.0	77.7	1.24 : 1
2	4.6	5.1	90.3	0.54 : 1
3	2.3	5.5	42.7	0.21 : 1
4	5.7	7.0	88.3	0.52 : 1
5	2.5	39.0	48.5	0.30 : 1
6	12.0	12.6	75.4	1.25 : 1
7	16.6	19.2	64.2	1.6 : 1

### *Discussion of Results.*

It will be noticed from the curves that in no case is the selective combustion of carbon monoxide in hydrogen perfectly complete; in all cases we are dealing with two simultaneous reactions, the oxidation of hydrogen and of carbon monoxide, the velocity of each naturally varying with the temperature, the composition of the gas, and also with the nature of the catalytic material employed.

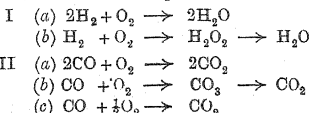
The results do not appear compatible with the theory of an intermediate compound as interpreted in the older sense and not on Langmuir's view of surface combination, since no evidence of stable hydrides or carbonyls was obtained. The results, in addition, do not favour the adsorption theory of catalysis, for the following reasons.

Assuming that the reaction velocity is governed entirely by the rate of diffusion of the reactants through the atmosphere of carbon dioxide and steam around the material, then the relative reaction velocities, at any definite temperature, should not change to any marked extent with the nature of the catalytic material employed,

and, further, owing to the greater mobility of hydrogen, this gas should burn more quickly than carbon monoxide, especially at relatively low temperatures, when the adsorbed atmosphere is presumably denser than at more elevated temperatures. Neither of these deductions is confirmed by the experimental figures.

The general shape of the temperature:ratio curves obtained can, however, be deduced from theoretical considerations if Langmuir's theory of single layer absorption is adopted, together with Lewis's application of the Marcelin-Rice principle of activation to heterogeneous systems.

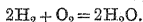
It is evident that the dependence of the ratio  $\text{CO}:\text{H}_2$  burnt, on the partial pressure of the reactants on a given catalyst at a definite temperature, indicates the relative reaction velocities of two separate reactions, the surface oxidation of hydrogen and of carbon monoxide; these can be expressed in the form:



Lewis gives evidence in favour of assuming that in the case of the combustion of hydrogen the primary reaction is



supported to some extent by the work of Bone and Wheeler (*Phil. Trans.*, 1906, [A], 206, 1), who disagree with Bodenstein (*Zeitsch. physikal. Chem.*, 1899, 29, 665), whose figures for the velocity constant corresponded with the reaction



In the present instance, where ratios alone are being considered, we can easily distinguish between these reactions, since if each reaction follows the same course, for example. I (a) and II (a), then, since

$$\begin{array}{l} 2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O} \\ 2\text{CO} + \text{O}_2 = 2\text{CO}_2 \\ -\frac{dc_{\text{H}_2}}{dt} = (\text{H}_2)^2(\text{O}_2) \end{array}$$

and

$$-\frac{dc_{\text{CO}}}{dt} = (\text{CO})^2(\text{O}_2)$$

or

$$\begin{array}{l} -\frac{dc_{\text{CO}}}{dt} \\ -\frac{dc_{\text{H}_2}}{dt} \end{array} = \frac{(\text{CO})^2}{(\text{H}_2)^2}$$

that is, the relative velocities of combustion are independent of the concentration of oxygen.

If, on the other hand, the oxidation of hydrogen and carbon monoxide proceeds differently, say according to the equations I (b) and II (c), then, since

$$\begin{aligned} \text{H}_2 + \text{O}_2 &\rightarrow \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} \\ \text{CO} + \frac{1}{2}\text{O}_2 &\rightarrow \text{CO} \end{aligned}$$

$$\frac{-\frac{dc_{\text{CO}}}{dt}}{-\frac{dc_{\text{H}_2}}{dt}} = \frac{(\text{CO})(\text{O}_2)^{\frac{1}{2}}}{(\text{H}_2)(\text{O}_2)} = \frac{(\text{CO})}{(\text{H}_2)(\text{O}_2)^{\frac{1}{2}}}$$

that is, the relative rates will be a function of the pressure of oxygen. From the above experimental determinations, all the possible ratios can be calculated. A few trials were sufficient to indicate that one ratio, and one ratio only, gave figures closely approximating to those experimentally determined, namely,

$$\frac{-\frac{dc_{\text{CO}}}{dt}}{-\frac{dc_{\text{H}_2}}{dt}} = \frac{(\text{CO})}{(\text{H}_2)(\text{O}_2)^{\frac{1}{2}}}$$

and the experimental and calculated values are given in the following table:

Expt. No.	Ratio: $\frac{\text{CO} : \text{H}_2 \text{ (Expt. I.)}}{\text{CO} : \text{H}_2 \text{ (Expt. II.)}}$ of gases burnt.	Ratio: $\frac{(\text{CO})}{(\text{H}_2)(\text{O}_2)^{\frac{1}{2}}} \text{ (Expt. I.)}$ $\frac{\text{CO}}{(\text{H}_2)(\text{O}_2)^{\frac{1}{2}}} \text{ (Expt. II.)}$ calculated from compositions of mixtures.
1	2.3	2.28
2	2.6	3.0
3	0.40	0.30
4	1.7	2.9
5	0.24	0.19
6	0.77	0.76
7		

It will be observed that, with the exception of the ratio expt. 4:5, the agreement is fairly good between the observed figures and those calculated on the assumption that the velocities of reaction are in accordance with one of the two following schemes:

- A.  $\begin{cases} \text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} \\ \text{CO} + \frac{1}{2}(\text{O}_2) \rightarrow \text{CO}_2 \end{cases}$
- B.  $\begin{cases} \text{H}_2 + \frac{1}{2}(\text{O}_2) \rightarrow \text{H}_2\text{O} \\ \text{CO rate independent of the concentration of oxygen.} \end{cases}$

Although from these experiments it is impossible to distinguish between these two hypothetical cases, yet, in view of the fact that carbon monoxide is burnt on all the catalysts investigated, whether

oxides or not, it may be assumed that the first set of reactions is probably more correct, which on Langmuir's hypothesis would indicate that the hydrogen and carbon monoxide were bound by only one valency bond to the catalytic material, and the oxygen both by one and by two.

Lewis adopts the hypothesis that the oxygen is adsorbed by the catalyst and exists in the atomic state on its surface, and that all that is necessary is for an activated molecule of hydrogen or carbon monoxide to come into contact with an atom of oxygen. If we adopt the hypothesis that the number of active oxygen atoms or molecules are already present in large excess, and that the reaction velocity is governed entirely by the number of molecules of hydrogen or carbon monoxide that receive the necessary critical energy increment per second, then the ratio of gases burnt should be independent of the concentration of oxygen, which is not the case. It would appear, however, that the energy necessary to activate a gram-molecule of oxygen sufficiently for it to become reactive at the surface of such catalysts is extremely small, and for the purposes of calculation may be neglected.

The reaction velocity of each reaction is accordingly given by the expressions

$$-\frac{dc_{CO}}{dt} = ae^{-\frac{(Nh\nu_{CO} + L_{CO_2})}{RT}}$$

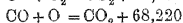
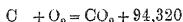
$$-\frac{dc_{H_2}}{dt} = a'e^{-\frac{(Nh\nu_{H_2} + L_{H_2O})}{RT}}$$

or

$$\frac{-\frac{dc_{CO}}{dt}}{-\frac{dc_{H_2}}{dt}} = \frac{a}{a'} e^{\frac{Nh\nu_{H_2} - Nh\nu_{CO} + L_{H_2O} - L_{CO_2}}{RT}}$$

where  $\nu_{CO}$ ,  $\nu_{H_2}$  are the frequencies of the radiation bringing about the partial activation of hydrogen and carbon monoxide,  $N$  the number of molecules per gram-molecule,  $h$  Planck's constant,  $L_{H_2O}$  and  $L_{CO_2}$  the heat of desorption per gram-molecule of the products of the reaction, namely, water and carbon dioxide at the temperature  $T$ ,  $\frac{a}{a'}$  the ratio of the surface concentrations of carbon monoxide and hydrogen. For the purposes of calculation,  $L_{H_2O}$  and  $L_{CO_2}$  are taken as the latent heats of water and carbon dioxide at the respective temperatures, it being assumed that the values alter in a linear manner with the temperature. For water, the values adopted are 9000 calories at  $100^\circ$  and 0 at  $365^\circ$ , the critical

point; for carbon dioxide, 6200 calories at  $0^\circ$  and 0 at  $35^\circ$ . Lewis's value, deduced from Bohr's atomic model of 21,000 calories per gram-molecule, is taken as the experimental value of  $Nh\nu_{H_2}$ , whilst that for carbon monoxide was calculated as follows. Assuming the equality of the four carbon linkings in the carbon atom, then from the heats of combustion of carbon and its oxide:



or the heat equivalent of two carbon-oxygen linkings is

$$68,220 - 26,100 = 42,120 \text{ calories,}$$

or 21,060 for one valency.

If we assume that the carbon monoxide is activated by desorption after adsorption on to the oxide catalyst by means of one carbon-oxygen valency, the necessary critical increment for such an activation is 21,060 calories per gram-molecule, or

$$Nh\nu_{CO} = 21,060.$$

Therefore  $Nh\nu_{H_2} - Nh\nu_{CO} = -60$  calories only, or the spectral regions in which hydrogen and carbon monoxide are activated are practically identical. An approximately similar result may be obtained from the ionising potentials of the two gases. It can easily be shown that the critical increment  $Nh\nu$  is equal to  $2.2 \times 10^4 V$  (where  $V$  is the ionising potential in volts). The value of  $V$  for hydrogen is approximately 16 and for carbon monoxide about 15.8 to 15.9 volts; thus, in this case,  $Nh\nu_{H_2} - Nh\nu_{CO} = +3000$  calories. These figures are necessarily somewhat inexact, and the degree of activation required for catalytic chemical reaction is probably much less than is required for ionisation, as indicated by the above figures.

The following table summarises the results of the calculation for the determination of the ratio of the reaction velocities at various temperatures, on the assumption that the activation of the oxygen is not a part of the process.

Temperature.	$L_{H_2O}$ .	$L_{CO_2}$ .	$\frac{-60 + L_{H_2O} - L_{CO_2}}{RT}$	$\frac{-60 + L_{H_2O} - L_{CO_2}}{RT} e^{\epsilon}$
$-50^\circ$	14,500	18,000	-9.0	0.0001
0	12,500	6,000	11.8	135,000
50	10,800	0	16.6	$16 \times 10^6$
100	9,000	—	12.0	205,000
200	5,500	—	5.7	300
250	3,900	—	3.7	40.5
300	2,000	—	1.7	5.5
350	500	—	0.35	1.42
400	0	—	-0.04	0.96

The relative velocities of combustion for a mixture of carbon monoxide and hydrogen in the ratio of 1:8, calculated from the above table, are shown in the curve, and the similarity in form between this derived curve and that experimentally determined on the iron oxide catalyst is clearly indicated. A closer agreement is scarcely to be expected, since the factor introduced by the possible activation of the oxygen and the effect of its partial pressure on the reaction velocity have been neglected, together with the uncertainty introduced by equating the latent heat with the heat of desorption. It follows that the removal of carbon monoxide from hydrogen by this means takes place most readily at about  $50^{\circ}$  to  $100^{\circ}$ , whilst below  $-50^{\circ}$  and above  $400^{\circ}$  hydrogen burns more quickly than carbon monoxide, selective combustion being entirely dependent on the fact that energy is required for the desorption of one of the products of combustion, namely, water vapour, although in the case of iron oxide it is scarcely sufficiently reactive below  $220^{\circ}$  to permit of the optimum conditions of operation.

It is interesting to note that at high temperatures hydrogen burns more quickly than carbon monoxide.

It is evident that the simple adsorption theory, where the hydrogen and carbon monoxide are adsorbed and activated by radiation and the oxygen is adsorbed and activated by the catalyst, gives an adequate explanation for the observed dependence of the reaction velocity ratios on the composition of the gas and on the influence of temperature, but these considerations do not give any insight into the dependence of the ratio on the composition of the catalyst.

The temperature-coefficients of both these reactions are sufficiently large to exclude the hypothesis that every hydrogen and carbon monoxide molecule striking the surface and becoming attached to the catalyst is oxidised; one is forced to assume that the ratio  $\frac{a}{a'}$ , which is the ratio of the surface concentrations of the two gases, varies with the catalytic material. Adopting the hypothesis of molecular attachment by one bond for hydrogen and carbon monoxide, the ratio of the surface concentrations can be derived by Langmuir's equation:

$$\frac{N}{N_0} a = \frac{\sigma \mu}{1 + \sigma \mu}$$

where  $N$  = Avogadro's constant.

$N_0$  = number of space lattices per sq. cm.

$\sigma = \frac{A}{V}$ , where  $V$  = rate of evaporation from a completely



covered surface;  $A$ , a factor approximating to unity, being the fraction of the number of molecules striking the surface which are absorbed.

$\mu$  = gram-molecules striking.

$= K \frac{P}{\sqrt{MT}}$ , where  $P$  is the gas pressure,  $M$  the molecular

weight, and  $T$  the absolute temperature.

$\alpha$  = gram-molecules adsorbed per unit area.

Hence

$$\begin{aligned} \frac{\alpha_{\text{CO}}}{\alpha_{\text{H}_2}} &= \frac{\sigma_1 \mu_1 (1 + \sigma_2 \mu_2)}{\sigma_2 \mu_2 (1 + \sigma_1 \mu_1)} \\ &= \frac{P_{\text{CO}} A_{\text{CO}} (V_{\text{H}_2} \sqrt{M_{\text{H}_2} T} + A_{\text{H}_2} P_{\text{H}_2})}{P_{\text{H}_2} A_{\text{H}_2} (V_{\text{CO}} \sqrt{M_{\text{CO}} T} + A_{\text{CO}} P_{\text{CO}})} \end{aligned}$$

Putting  $A_{\text{CO}} = A_{\text{H}_2}$ ,

$$\frac{\alpha_{\text{CO}}}{\alpha_{\text{H}_2}} = \frac{P_{\text{CO}} (V_{\text{H}_2} \sqrt{M_{\text{H}_2} T} + A P_{\text{H}_2})}{P_{\text{H}_2} (V_{\text{CO}} \sqrt{M_{\text{CO}} T} + A P_{\text{CO}})}$$

whilst if each molecule is attached by two bonds,

$$\frac{\alpha_{\text{CO}}}{\alpha_{\text{H}_2}} = \frac{\sqrt{\sigma_1 \mu_1}}{\sqrt{\sigma_2 \mu_2}} = \sqrt{\frac{V_{\text{H}_2} P_{\text{CO}} \sqrt{M_{\text{H}_2}}}{V_{\text{CO}} P_{\text{H}_2} \sqrt{M_{\text{CO}}}}}$$

We have assumed in the former calculation that the surface concentration ratio  $\frac{\alpha}{\alpha'}$  is equal to the ratio

$$K \frac{P_{\text{CO}}}{P_{\text{H}_2}} \cdot \frac{V_{\text{H}_2}}{V_{\text{CO}}}$$

(where  $K$  is a constant), which is actually the case for any one particular catalytic material, but a closer approximation is given by

$$\frac{\alpha}{\alpha'} = K \frac{P_{\text{CO}}}{P_{\text{H}_2}} \cdot \frac{V_{\text{H}_2}}{V_{\text{CO}}}$$

where  $V_{\text{H}_2}$  is the rate of evaporation of hydrogen from a completely covered surface. In the cases considered, where we are dealing with the evaporation of a gas from a solid surface, the rate of evaporation from a completely covered surface may be regarded as a simple function of the vapour pressure. It follows that for various surfaces the rates of evaporation of gases are not the same, and we must postulate, as Langmuir has done, quasi-chemical combination between gas and surface, these quasi-chemical combinations possessing different free energies. Since little is known about the unstable hydrides of the elements, the work of Sieverts (*Zeitsch. physikal. Chem.*, 1907, 60, 169, *et seq.*; see

also D. P. Smith, *J. Physical Chem.*, 1918, **23**, 186) being devoted to the study of occlusion of this gas in the various metals, we may, for purposes of comparison, regard the free energies of the unstable quasi-chemical superficial hydrides or carbonyls as equal or running parallel to their heats of formation and stability, whilst a knowledge of the vapour pressures at different temperatures and the specific heats is required for an exact determination of the free energy at various temperatures.

It will be noted that the ratio  $H_2/CO$  burnt increases progressively with the following catalytic materials: iron oxide; iron oxide with promoters; copper oxide; nickel; palladium; this is the order of increase in the stability of the hydrides, the union of palladium and hydrogen being actually exothermic at the ordinary temperature. The rate of evaporation of hydrogen from these surfaces,  $V_{H_2}$ , will therefore, under identical conditions, decrease in the above order, or the surface concentration,  $\alpha_{H_2}$ , will increase. Hence the ratio  $\alpha_{CO}/\alpha_{H_2}$ , which is the ratio of the surface concentrations of the two gases, will alter with the catalytic material, and with this alteration in the surface concentrations there will be a corresponding alteration in the rates of combustion. As the temperature is raised, the rates of evaporation of the gases increase, and thus the specific influence of the catalytic material disappears; this inference is clearly indicated in the curves, where it will be noted that at  $400^\circ$  the ratio is practically independent of the catalyst employed.

#### *Summary.*

The selective combustion of carbon monoxide in hydrogen on the surface of catalytic materials is shown to be a case of two simultaneous reactions. The rates of combustion of the two gases between  $100^\circ$  and  $400^\circ$  are related to the composition of the gaseous mixture by the expression:

$$\frac{-\frac{dc_{CO}}{dt}}{-\frac{dc_{H_2}}{dt}} = K \frac{(CO)}{(H_2)(O_2)^{\frac{1}{2}}}.$$

Elevation in temperature causes a decrease in the apparent selective character of the reaction, and the relationship between the influence of temperature and the ratio of gases burnt can be calculated approximately from the conception of the critical increment as developed by Lewis.

The results obtained are in agreement with Langmuir's theory of adsorption, in which the adsorbed layer is considered to be only

one molecule thick; but the surface concentration of each gas is found to be dependent, not only on the nature of the gas, but also of the absorbing surface, indicating that the quasi-chemical combinations between gas and surface possess different free energies and are not simply the result of differences in activation of the reacting gaseous constituents.

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### LXXXV.—*The Temperature of Explosion for Endothermic Substances.*

By RASIK LAL DATTA and NIHAR RANJAN CHATTERJEE.

BERTHELOT has shown (*Compt. rend.*, 1887, 105, 1159; 1899, 129, 926) that certain endothermic substances which, if heated gradually, would either volatilise or decompose, can be made to explode by throwing them into a vessel previously raised to a suitably high temperature. This result was observed with trinitrophenol, mono-, di-, and tri-nitronaphthalene, and potassium chlorate. The authors, following up these observations of Berthelot, find that for each endothermic substance there is a temperature below which explosive decomposition does not occur, and this definite point is termed the temperature of explosion.

The procedure adopted was to drop a small quantity of the substance to the bottom of a clean test-tube immersed in a bath of potassium hydrogen sulphate just when the temperature of the bath has attained the temperature particular to each substance, as otherwise a simple decomposition would take place. The temperature of this bath, up to 500°, was recorded on a mercury thermometer; at higher temperatures, a thermo-couple was employed. The experiment was carried out in an atmosphere of carbon dioxide, but any other indifferent gas, such as nitrogen, may be used, and explosive decomposition occurs with equal readiness in a vacuum.

From the results recorded below for the temperatures of explosion of various substances, one or two conclusions of a general kind may be drawn. So far as nitro-derivatives are concerned, it appears that, of the disubstituted derivatives of benzene, the ortho-compound, as a rule, has the lowest, and the para-compound the highest, temperature of explosion. Thus the temperatures of explosion for *o*-, *m*-, and *p*-chloronitrobenzene are 614°, 638°, and

720° respectively. In the case, however, of the nitrophenols, the para-compound has a lower temperature of explosion than the meta-compound. For dinitro-compounds with the nitro-group in the meta-position, the temperature of explosion falls as the number of alkyl groups attached to the ring increases. In this connexion, the figures for the temperatures of explosion of *m*-dinitrobenzene, 2:4-dinitrotoluene, and 4:6-dinitro-*o*-xylene may be quoted: they are 580°, 470°, and 438° respectively. The same relation holds good in the case of trinitro-derivatives.

In the following record, the temperature of explosion follows the name of the compound examined.

#### *Nitro-compounds.*

*o*-Dinitrobenzene, 472°; *m*-dinitrobenzene, 580°; 1:3:5-trinitrobenzene, 520°; 2:4-dinitrotoluene, 470°;  $\alpha$ -2:4:6-trinitrotoluene, 418°; 4:6-dinitro-*o*-xylene, 438°; 3:4-dinitro-*o*-xylene, 413°; trinitroxylene (m. p. 178°), 408°; 2:4:6-trinitro-*m*-xylene, 410—412°; 2:3:6-trinitro-*p*-xylene, 410°; dinitromesitylene, 418°; trinitromesitylene, 415°; trinitrocumene, 502°; 2:4-dinitrostilbene, 412°; *o*-dinitrostilbene, 420°;  $\alpha$ -dinitrodiphenylmethane (m. p. 181°), 335°; 1:6-dinitronaphthalene, 492°; 1:8-dinitronaphthalene, 445°; trinitronaphthalene (m. p. 122°), 364°; tetranitronaphthalene (m. p. 170°), 323°; *o*-chloronitrobenzene, 614°; *m*-chloronitrobenzene, 638°; *p*-chloronitrobenzene, 720°; *p*-bromonitrobenzene, 755°; *p*-iodonitrobenzene, 605°; *o*-nitroaniline, 655°; *m*-nitroaniline, 552°; *p*-nitroaniline, 627°; 2:4-dinitroaniline, 548°; *p*-nitrobenzoic acid, 635°; 2:4-dinitrobenzoic acid, 484°; 3:5-dinitrobenzoic acid, 523°; *o*-nitrophenol, 630°; *m*-nitrophenol, 657°; *p*-nitrophenol, 633°; 2:4-dinitrophenol, 498°; 2:4:6-trinitrophenol, 418°; 3-nitro-*o*-cresol, 503°; 6-nitro-*m*-cresol, 398°; 3:4-dinitro-*o*-cresol, 472°; 3:5-dinitro-*o*-cresol, 455°; 2:4:6-trinitro-*m*-cresol, 405°; 5-nitro-*p*-xylenol, 407°; 3:5-dinitro-*o*-xylenol, 432°; 2:4:6-trinitroresorcinol, 314°; *o*-dinitrodihydroxydiphenyl (m. p. 184°), 447°; 2:6-dichloro-4-nitrophenol, 548°; 4:6-dichloro-2-nitrophenol, 562°; 2:6-dibromo-4-nitrophenol, 625°; 4:6-dibromo-2-nitrophenol, 630°; 2:4:6-tribromo-3-nitrophenol, 605°; 6-bromo-2:4-dinitrophenol, 713°; 2-iodo-3-nitrophenol, 448°; 2:4-di-iodo-6-nitrophenol, 533°; 2:6-di-iodo-4-nitrophenol, 548°.

#### *Picrates.*

Ammonium picrate, 423°; hydrazine picrate, 385°; allylamine picrate, 270°; carbamide picrate, 489°; semicarbazide picrate,

474°; guanidine picrate, 498°; hexamethylenetetramine picrate, 360°; aniline picrate, 398°; *o*-toluidine picrate, 400°;  $\alpha$ -naphthol picrate, 458°;  $\beta$ -naphthol picrate, 469°; naphthalene picrate, 484°; phenanthrene picrate, 478°; acenaphthene picrate, 418°; pyridine picrate, 432°; quinine picrate, 280°; quinidine picrate, 272°; cinchonine picrate, 268°; cinchonidine picrate, 260°; strychnine picrate, 290°; atropine picrate, 460°.

#### *Azo-compounds.*

Azobenzene, 540°; aminoazobenzene, 598°; dimethylaminoazobenzene, 643°; diazoaminobenzene, 703°.

#### *Haloid Compounds.*

Iodoform, 295°; *p*-di-iodobenzene, 788°; 2:4:6-tri-iodophenol, 675°; di-iodo-*o*-cresol, 782°; 2:4:6-tri-iodo-*m*-cresol, 696°; 2:4:6-tribromoresorcinol, 713°; 2:4:6-tribromo-*o*-rcinol, 793°; penta-bromo-*o*-rcinol, 698°.

#### *Organic Perchlorates.*

Allylamine perchlorate, 262°; methylamine perchlorate, 338°; propylamine perchlorate, 290°; heptylamine perchlorate, 265°; hexylamine perchlorate, 278°; aniline perchlorate, 250°.

*o*-Toluidine perchlorate.—This salt has not previously been described. It is prepared by neutralising the base with perchloric acid. It does not melt on heating, but slowly carbonises:

0.0993 gave 6 c.c.  $N_2$  at 28° and 760 mm.  $N=6.72$ .

$C_7H_9N, HClO_4$  requires  $N=6.76$  per cent.

It explodes at 260°.

*m*-Toluidine perchlorate.—This salt was prepared by the interaction of the hydrochloride of the base and silver perchlorate. It melts and chars at 200°:

0.0804 gave 4.9 c.c.  $N_2$  at 28° and 760 mm.  $N=6.78$ .

$C_7H_9N, HClO_4$  requires  $N=6.76$  per cent.

It explodes at 300°.

The following perchlorates were prepared by double decomposition, as in the preceding case.

*p*-Toluidine perchlorate:

0.1027 gave 6.2 c.c.  $N_2$  at 29° and 760 mm.  $N=6.70$ .

$C_7H_9N, HClO_4$  requires  $N=6.76$  per cent.

It explodes at 278°.

*m*-4-*Xylidine perchlorate* decomposes at 200° :

0.1000 gave 5.8 c.c.  $N_2$  at 28° and 760 mm.  $N=6.45$ .

$C_8H_{11}N, HClO_4$  requires  $N=6.33$  per cent.

It explodes at 260°.

*p*-*Xylidine perchlorate* decomposes at 210° :

0.1072 gave 6 c.c.  $N_2$  at 28° and 760 mm.  $N=6.33$ .

$C_8H_{11}N, HClO_4$  requires  $N=6.33$  per cent.

It explodes at 258°.

*Benzylamine perchlorate* melts at 120° :

0.0816 gave 5.2 c.c.  $N_2$  at 28° and 760 mm.  $N=7.02$ .

$C_7H_9N, HClO_4$  requires  $N=6.76$  per cent.

It explodes at 305°.

*Phenylethylamine perchlorate*, 280°;  $\alpha$ -*naphthylamine perchlorate*, 228°; *menthylamine perchlorate*, 308°.

*Camphylamine perchlorate* melts and decomposes at 276° :

0.0570 gave 3.1 c.c.  $N_2$  at 29° and 760 mm.  $N=5.97$ .

$C_{10}H_{19}N, HClO_4$  requires  $N=5.53$  per cent.

It explodes at 255°.

*Diethylamine perchlorate* melts at 107° and is very hygroscopic :

0.1067 gave 7.8 c.c.  $N_2$  at 28° and 760 mm.  $N=8.13$ .

$C_4H_{11}N, HClO_4$  requires  $N=8.09$  per cent.

It explodes at 282°.

*Diisopropylamine perchlorate*, 308°; *diamylamine perchlorate*, 323°; *benzylethylamine perchlorate*, 322°; *benzylmethylamine perchlorate*, 294°.

*Dibenzylamine perchlorate* explodes at 290° :

0.0574 gave 2.6 c.c.  $N_2$  at 27° and 760 mm.  $N=5.31$ .

$C_{14}H_{19}N, HClO_4$  requires  $N=4.7$  per cent.

*p*-*Tolyltrimethylammonium perchlorate* melts at 192° :

0.0670 gave 3.8 c.c.  $N_2$  at 30° and 760 mm.  $N=6.08$ .

$C_{10}H_{16}N, ClO_4$  requires  $N=5.62$  per cent.

It explodes at 310°.

*Methylpyridinium perchlorate* explodes at 362° :

0.0661 gave 4.9 c.c.  $N_2$  at 32° and 760 mm.  $N=8.12$ .

$C_6H_9N, ClO_4$  requires  $N=7.61$  per cent.

*Ethylpyridinium perchlorate* explodes at 340° :

0.0765 gave 4.9 c.c.  $N_2$  at 30° and 760 mm.  $N=7.07$ .

$C_7H_{11}N, ClO_4$  requires  $N=6.73$  per cent.

*Neurine perchlorate*, 298°; *phenylbenzylmethylammonium perchlorate*, 275°; *trimethylsulphonium perchlorate*, 280°; *ethylquinolinium perchlorate*, 330°; *propylquinolinium perchlorate*,

342°; ethylquinaldinium perchlorate, 268°; hydrazine monoperchlorate, 238°; hydrazine diperchlorate, 215°; trimethylenediamine perchlorate, 310°; ethylenediamine perchlorate, 270°.

*Guanidine perchlorate* melts at 237°:

0.2249 gave 53 c.c.  $N_2$  at 29° and 760 mm.  $N=26.15$ .

$CH_5N_3.HClO_4$  requires  $N=26.41$  per cent.

It explodes at 367°.

*Semicarbazide perchlorate* explodes at 278°:

0.0929 gave 20.2 c.c.  $N_2$  at 30° and 760 mm.  $N=24.01$ .

$CH_5ON_3.HClO_4$  requires  $N=24.00$  per cent.

*Piperazine perchlorate* melts at 80°:

0.1156 gave 9 c.c.  $N_2$  at 29° and 760 mm.  $N=8.64$ .

$C_4H_{10}N_2.2HClO_4.2H_2O$  requires  $N=8.69$  per cent.

It explodes at 290°.

*o-Phenylenediamine perchlorate* explodes at 250°:

0.0310 gave 2.6 c.c.  $N_2$  at 27° and 760 mm.  $N=9.31$ .

$C_6H_8N_2.2HClO_4$  requires  $N=9.09$  per cent.

*m-Phenylenediamine perchlorate*, 263°; *p-phenylenediamine perchlorate*, 260°.

#### *Alkaloids, etc.*

Brucine, 793°; narcotine, 720°; narceine, 697°; chloralurethane, 673°; oxalylhydrazide, 548°; acetophenoneoxime, 734°; benzil, 643°.

Investigations on similar lines are being continued.

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### LXXXVI.—*The Preparation of Butylamine and of n-Dibutylamine. The Separation of Aliphatic Amines by Partial Neutralisation.*

By EMIL ALPHONSE WERNER.

THE preparation of *n*-butylamine, and of *n*-dibutylamine, from the interaction of butyl bromide and ammonia in alcoholic solution at the ordinary temperature has been investigated. A procedure similar to that employed in the preparation of the corresponding ethyl derivatives of ammonia was adopted (T., 1918, 113, 899).

The details of a few experiments on a simple method for the separation of amines from intermediate distillates are recorded, and whilst the results have a practical value as regards the economic preparation of amines on a large scale, they go to show that the prevailing views with respect to the relative basicity of primary, secondary, and tertiary aliphatic amines require to be modified. (Expts. 2, 3, and 4.)

### EXPERIMENTAL.

*n*-Butyl bromide was conveniently prepared by distillation at 98–100° of a mixture of butyl alcohol, sulphuric acid, and sodium bromide in molecular proportions, the temperature being raised to 120° towards the end of the process. The yield of the crude product, dried over calcium chloride, was equal to 92 per cent. of the theoretical, and from 1126 grams there were obtained after redistillation 1082 grams of pure butyl bromide, boiling at 100–101°.

*Expt. I.*—Four litres of 90 per cent. alcohol were saturated with ammonia until 500 grams of the gas had been dissolved; 200 grams of butyl bromide were added (ratio butyl bromide to  $\text{NH}_3$  approximately 1 to 20), after which, at successive intervals of three days, fresh quantities of the alkyl haloid were added as follows: 180, 170, 160, 150, and finally 140 grams. Thus, in all, 1000 grams were added over a period of fifteen days; preliminary tests had shown that nearly all of the butyl bromide was decomposed after three days. Only a few crystals of ammonium bromide separated, and on the twentieth day the alcoholic solution was concentrated by distillation, when 175 grams of ammonium bromide were recovered. As no crystalline matter separated after further concentration, the product was diluted with water and boiled to expel the last traces of alcohol. A dark brown, syrupy liquid (1200 grams) was ultimately obtained, which, analysis showed, contained 399.4 grams of bromine; hence this required 200 grams of sodium hydroxide for the liberation of the total amines present.

Whilst the separation of butylamine (b. p. 76°) from dibutylamine (161°) by distillation was comparatively simple, this was not so as regards the separation of the latter from tributylamine (214°). Hence, in order to avoid tedious fractionations of a mixture of all three amines, fractional treatment with sodium hydroxide was adopted as a preliminary (T., *loc. cit.*).

The product was introduced into a large separating funnel, 40 grams of sodium hydroxide dissolved in 80 c.c. of water were added, and the mixture was vigorously agitated at intervals; after a few hours the layer of 'amine' which had separated was removed.



It weighed 67 grams (dry) and was a mixture of di- and tri-butylamine, in which the latter largely predominated; it was dealt with as described later. (Amine A, Expt. 2.)

After the addition of 80 grams of sodium hydroxide to the residual liquid, followed by brisk agitation, 200 grams of 'amine' (B) were separated. This was distilled, with the aid of a three-bulb pear-shaped still-head, and 109 grams of pure dibutylamine were collected, after 49 grams had passed over between  $80^{\circ}$  and  $158^{\circ}$  (dealt with under Expt. 3). The residue, 42 grams, boiling above  $161^{\circ}$  was added to 'amine' (A). To the remaining solution a final quantity of 80 grams of sodium hydroxide was added, the mixture was transferred to a flask, and the whole of the liberated amine was removed by distillation at  $90^{\circ}$ . The product, 'amine' (C), weighed 187 grams (dry); it was redistilled, using a three-column evaporator still-head, and 167 grams of pure butylamine ( $76-77^{\circ}$ ) were collected. The residue (20 grams) was added to the first distillate (49 grams) from 'amine' (B).

*Separation of a Mixture of Dibutylamine and Tributylamine,  
by Partial Neutralisation with Hydrochloric Acid.*

The separation of the mixture of 'amine' (A) with the residue from 'amine' (B) into its constituents by fractional distillation was abandoned as hopeless; thus, for example, whilst the greater part passed over before the boiling point ( $214^{\circ}$ ) of tributylamine was reached, the first fraction ( $162-180^{\circ}$ ) contained 10.7 per cent. of tributylamine, and the last fraction ( $200-214^{\circ}$ ) contained 16.6 per cent. of dibutylamine.

The following simple procedure gave the desired result:

*Expt. 2.*—The mixture, 98 grams, which on analysis was found to contain 51 grams of dibutylamine, was placed in a separating funnel and 132 c.c. of 3*N*-hydrochloric acid\* and 40 c.c. of water were added. The product was thoroughly agitated, and after a few hours the layer of insoluble amine was removed. It weighed 46 grams, and distilled steadily at  $212-214^{\circ}$ ; it was therefore pure tributylamine.

The aqueous solution was evaporated at  $100^{\circ}$ , and the residue dried over sulphuric acid; it weighed 64.3 grams and contained  $\text{Cl} = 21.46$ , whilst  $(\text{C}_4\text{H}_9)_2\text{NH}\cdot\text{HCl}$  requires  $\text{Cl} = 21.45$  per cent.

The separation of the two amines was therefore complete.

\* The amount of hydrochloric acid required to combine with the dibutylamine only; the extra water was necessary to keep the salt in solution.

*Separation of a Mixture of Butylamine and Dibutylamine by  
Partial Neutralisation with Hydrochloric Acid.*

*Expt. 3.*—The fraction collected between  $80^{\circ}$  and  $158^{\circ}$  (49 grams) from the distillation of 'amine' (B) and the residue (20 grams) from the distillation of 'amine' (C) were mixed. Analysis showed that the product contained approximately 48 grams of butylamine. It was well agitated with 220 c.c. of 3*N*-hydrochloric acid in a separating funnel and allowed to remain for twenty-four hours. The solution was extracted twice with 70 c.c. of ether to remove all the free amine. The ethereal solution (previously dried) was distilled, and after removal of the solvent and of a few c.c. of amine which passed over below  $161^{\circ}$ , 18 grams of pure dibutylamine were collected.

The aqueous solution was evaporated at  $100^{\circ}$ , and the residue dried over sulphuric acid. It contained  $\text{Cl}=31.14$ , whilst  $\text{C}_4\text{H}_9\cdot\text{NH}_2\cdot\text{HCl}$  requires  $\text{Cl}=32.42$  per cent. The weight was 74 grams, and the proportion of butylamine hydrochloride was equal to 86.2 per cent. Whilst the separation in this case was not so complete as in *Expt. 2*, the results show that on a manufacturing scale the recovery of amines from intermediate distillates and residues could be economically effected by this method.

The total yields of the respective amines were: butylamine, 215 grams = 40.2 per cent.; dibutylamine, 181 grams = 41.1 per cent.; and tributylamine, 47 grams = 10.4 per cent. of the theoretical. When 200 grams of butyl bromide were added to 3 litres of 90 per cent. alcohol, saturated with ammonia as in *Expt. 1*, and the product worked up after five days, 73 grams of butylamine, equal to 68.5 per cent. of the theoretical, were obtained; the yield of dibutylamine was 28 grams, equal to 31.9 per cent. of the theoretical, and no tributylamine was formed.

The following *n*-butyl derivatives were incidentally prepared in connexion with other work:

Ethyl *n*-butylcarbamate,  $\text{C}_4\text{H}_9\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ , from the interaction of butylamine and ethyl chloroformate dissolved in benzene, was obtained in theoretical yield as a colourless oil which boiled at  $202\text{--}203^{\circ}/765.5$  mm. (van Erp, *Rec. trav. chim.*, 1895, 14, 1, gives  $100^{\circ}/15$  mm.).

Dibutylcarbamyl chloride,  $(\text{C}_4\text{H}_9)_2\text{N}\cdot\text{COCl}$ , a colourless oil, which boiled at  $242\text{--}243^{\circ}/755$  mm., and became pink on exposure to air, was obtained from the interaction of carbonyl chloride and dibutylamine dissolved in benzene.

Tributylcarbamide,  $\text{C}_4\text{H}_9\cdot\text{NH}\cdot\text{CO}\cdot\text{N}(\text{C}_4\text{H}_9)_2$ , was obtained as a viscous, colourless liquid which boiled at  $238\text{--}239^{\circ}/766$  mm., by the

action of butylamine on the foregoing compound dissolved in benzene.

as-Dibutylcarbamide,  $\text{NH}_2 \cdot \text{CO} \cdot \text{N}(\text{C}_4\text{H}_9)_2$ .—The preparation of this derivative furnished an interesting example of the use of benzene in obtaining an anhydrous solid as described by Atkins and Wilson (T., 1915, 107, 916); and the details are perhaps worth recording. Potassium cyanate was added to an aqueous solution of dibutylamine hydrochloride, and a viscous oil separated rapidly when the solution was heated to  $100^\circ$ . The oil, which was readily soluble in alcohol, ether, chloroform, or benzene, showed no signs of crystallisation\* after it had remained for three days in a desiccator over sulphuric acid. The addition of light petroleum to the cold solution in benzene failed to induce crystallisation, and with the object of removing the solvent the mixture was distilled from a flask plunged in hot water. When a portion of the solvent had passed over as a turbid mixture, a sudden copious separation of needle-shaped crystals, melting at  $149\text{--}150^\circ$ , took place, while the liquid was still warm.

Found:  $\text{N} = 16.11$ .  $\text{C}_9\text{H}_{20}\text{ON}_2$  requires  $\text{N} = 16.28$  per cent.

The compound is very hygroscopic; it liquefies after exposure to the air for a few minutes.

*Separation of Diethylamine from Triethylamine by Partial  
Neutralisation with Hydrochloric Acid.*

The following experiment supplies a further illustration of the use of this method.

Expt. 4.—In the preparation of a considerable quantity of diethylamine, a fraction was collected between  $75^\circ$  and  $91^\circ$ ; it had the composition  $\text{NH} \cdot \text{Et}_2 = 6.74$  per cent.,  $\text{N} \cdot \text{Et}_3 = 93.26$  per cent. It weighed 146 grams, and therefore contained 9.84 grams of diethylamine. It was mixed with 67 c.c. of 2*N*-hydrochloric acid and treated as described in Expt. 3.

The free amine was collected without loss and boiled at  $90\text{--}91^\circ$ , the boiling point of pure triethylamine.

The hydrochloride recovered from the aqueous solution contained  $\text{Cl} = 32.22$ , whilst  $(\text{C}_2\text{H}_5)_2\text{NH} \cdot \text{HCl}$  requires  $\text{Cl} = 32.42$  per cent.

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\* Monobutylcarbamide melts at  $86^\circ$ ; disubstituted carbamides of the above type generally melt at a much higher temperature than the monosubstituted derivatives.

LXXXVII.—*The Abnormal Behaviour of Glyoxaline-carboxylic Esters and Anilides towards Diazonium Salts.*

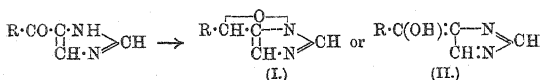
By ROBERT GEORGE FARGHER and FRANK LEE PYMAN.

In a recent paper (this vol., p. 217), we put forward evidence showing that glyoxalines are only capable of coupling with diazonium salts when they contain a free imino-group and also a hydrogen atom or some other displaceable group, such as the carboxyl group, in one of the 2-, 4-, or 5-positions. Numerous derivatives of glyoxaline, in which these conditions are fulfilled, have been shown to couple with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate, but an exceptional behaviour is shown by the esters of 5-methylglyoxaline-4-carboxylic acid (Gerngross, *Ber.*, 1912, 45, 513) and the esters of glyoxaline-4-carboxylic acid (Pyman, *T.*, 1916, 109, 186). These give a negative result, whereas the corresponding acids behave normally, giving deep red solutions with the reagent.

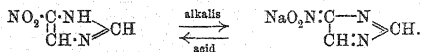
With the object of finding some clue to this abnormality, we have examined the behaviour of a number of carboxylic acids containing the glyoxaline nucleus and their esters towards sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate. All the acids examined gave a positive result, and so also did the esters of those acids, such as glyoxalineacetic acid, in which the carbonyl group is separated from the glyoxaline nucleus by a chain of one or more carbon atoms. The esters of the 2-alkylglyoxaline-4-carboxylic acids, however, like those of glyoxaline-4-carboxylic acid and 5-methylglyoxaline-4-carboxylic acid, gave a negative result, and so also did the anilides of glyoxaline-4-carboxylic acid and its 2-alkyl derivatives. In order to ensure that the difference in behaviour was not due to the particular conditions selected for the test, the action of benzene-diazonium chloride and *p*-nitrobenzenediazonium chloride on glyoxaline-4-carboxylic acid and ethyl glyoxaline-4-carboxylate was examined. In the presence of hydrochloric acid or acetic acid, neither of the derivatives coupled, whilst in the presence of sodium carbonate or sodium hydroxide the acid coupled but the ester did not.

The abnormality is thus seen to be connected with the direct attachment of the carboxyalkyl or carboxyanilide group to the glyoxaline nucleus, and would seem to be due to the mutual influence of the imino- and carbonyl groups.

Further than this we do not as yet feel able to offer any explanation of the abnormality. The fact that all the glyoxalinecarboxylic esters and anilides behave normally towards silver nitrate in ammoniacal solution, yielding insoluble silver salts, rules out any formula such as (I) not containing a free iminic or acidic hydrogen atom, whilst their stability towards potassium permanganate in acid solution would appear to indicate that they exist as true glyoxalines in the presence of mineral acids.



There is, however, the possibility of a molecular rearrangement, such as that represented by formula (II), taking place under the influence of alkalis. The nitroglyoxalines also fail to couple with diazonium salts, and here the explanation seems clear, since these compounds dissolve in alkalis with a yellow colour, yielding salts which are no doubt derived from the corresponding nitronic acids, as Windaus (*Ber.*, 1909, **44**, 758) has suggested, and no longer contain an imino-group.



The glyoxalinecarboxylic esters and anilides, however, yield colourless solutions with alkalis, and although, bearing in mind that the nitroglyoxalines themselves are colourless and their alkaline solutions only comparatively pale yellow, the lack of colour would alone seem insufficient to preclude a formula such as (II), we do not feel justified in advancing it as more than a possibility until further experimental evidence has been accumulated.

While seeking for comparable instances of the mutual influence of imino- and carbonyl groups, we have observed that whereas anthranilic acid couples with sodium diazobenzene-*p*-sulphonate or *p*-nitrobenzenediazonium chloride in sodium carbonate solution, ethyl anthranilate gives a negative result. Both, of course, couple in acid solution. Further, it is perhaps worth noting that whereas the hydrochloride of anthranilic acid is stable in aqueous solution, the hydrochlorides of its methyl and ethyl esters are readily hydrolysed in cold aqueous solution with liberation of the free ester (compare Kolbe, *J. pr. Chem.*, 1884, [ii], **30**, 474; Fränkel and Spiro, *Ber.*, 1895, **28**, 1686; E. and H. Erdmann, *Ber.*, 1899, **32**, 1213), and whilst *s*-ethylenebisanthranilic acid dissolves readily in dilute

mineral acids, the corresponding methyl ester is insoluble even in excess (Fränkel and Spiro, *loc. cit.*).

#### EXPERIMENTAL.

The esters described in this communication were prepared by boiling the acids with absolute alcohol saturated with hydrogen chloride. After removing the excess of alcohol and adding cold saturated aqueous potassium carbonate, the esters of the 2-alkylglyoxaline-4-carboxylic acids separated in a crystalline state. The other esters were extracted from the solutions by means of chloroform, and crystallised either as base or as hydrogen oxalate.

*Ethyl 2-methylglyoxaline-4-carboxylate* crystallises from ethyl acetate in clusters of fine, shimmering needles, which melt at 156° (corr.) and are anhydrous. It is sparingly soluble in water, but readily so in alcohol or ethyl acetate.

Found: C=54.3; H=6.7; N=17.9.

$C_7H_{10}O_2N_2$  (154.1) requires C=54.5; H=6.5; N=18.2 per cent.

The ester gives no coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution.

#### *2-Ethylglyoxaline-4-carboxylic Acid and its Derivatives.*

*2-Ethylglyoxaline-4-carboxyanilide* is prepared from 2-ethylglyoxaline-4:5-dicarboxylic acid in a yield amounting to 45 per cent. of the theoretical by the general method described in a previous communication (this vol., p. 217). It is readily soluble in alcohol but very sparingly so even in boiling water, from which it crystallises in clusters of fine needles; these are anhydrous and melt at 193° (corr.), sintering from 190°. It gives no coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution.

Found: C=66.6; H=5.8; N=19.2.

$C_{12}H_{13}ON_3$  (215.2) requires C=66.9; H=5.6; N=19.5 per cent.

*2-Ethylglyoxaline-4-carboxylic acid* is obtained in good yield by the hydrolysis of the corresponding anilide by dilute hydrochloric acid at 130°. It is readily soluble in hot water, but sparingly so in cold, and crystallises from the former in well-defined, prismatic needles which contain two molecules of water of crystallisation. After drying at 110°, it melts at 252° (corr.), sintering from 248°. It gives an immediate blood-red coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution.

Found, in air-dried acid: loss at 110°=20.7

$C_6H_8O_2N_2 \cdot 2H_2O$  requires 20.5 per cent.

In acid dried at  $110^{\circ}$ ,  $C=51.3$ ;  $H=5.7$ ;  $N=19.9$ .

$C_6H_8O_2N_2$  (140.1) requires  $C=51.4$ ;  $H=5.8$ ;  $N=20.0$  per cent.

The *picrate* crystallises from water in large, prismatic needles containing one and a-half molecules of water of crystallisation. After drying at  $60^{\circ}$  in a vacuum, it sinters above  $170^{\circ}$  and forms a turbid liquid, which becomes clear at about  $195^{\circ}$ .

Found, in air-dried salt,  $H_2O=6.9$ .

$C_6H_8O_2N_2 \cdot C_6H_3O_7N_3 \cdot 1\frac{1}{2}H_2O$  requires 6.8 per cent.

In dried salt,  $N=18.7$ .

$C_6H_8O_2N_2 \cdot C_6H_3O_7N_3$  (369.2) requires  $N=19.0$  per cent.

*Ethyl 2-ethylglyoxaline-4-carboxylate* crystallises from ethyl acetate, in which it is readily soluble, in prismatic needles which melt at  $129^{\circ}$  (corr.), and are anhydrous. It is readily soluble in alcohol, but sparingly so in water. It gives no coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution.

Found:  $C=56.8$ ;  $H=7.2$ ;  $N=16.5$ .

$C_8H_{12}O_2N_2$  (168.2) requires  $C=57.1$ ;  $H=7.2$ ;  $N=16.6$  per cent.

### *2-Phenylglyoxaline-4-carboxylic Acid and its Derivatives.*

*2-Phenylglyoxaline-4-carboxyanilide* is prepared by the action of boiling aniline on 2-phenylglyoxaline-4:5-dicarboxylic acid in a yield amounting to 74 per cent. of the theoretical. As it is practically insoluble in boiling water, it is left behind after the steam distillation somewhat contaminated by resinous impurities, which are readily removed by grinding and washing with ice-cold alcohol. It is sparingly soluble in alcohol or the other usual organic solvents, and separates from alcohol in minute, glistening needles, which melt at  $263^{\circ}$  (corr.) and are anhydrous. It gives no coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution.

Found:  $C=72.6$ ;  $H=5.3$ ;  $N=15.9$ .

$C_{16}H_{13}ON_3$  (263.2) requires  $C=73.0$ ;  $H=5.0$ ;  $N=16.0$  per cent.

*2-Phenylglyoxaline-4-carboxylic acid* is obtained in good yield by the hydrolysis of the corresponding anilide, which, however, is much more stable towards acid hydrolysis than the 2-alkyl derivatives. At  $130^{\circ}$  the reaction proceeds very slowly, but at  $145$ — $150^{\circ}$  the reaction is complete after eight to nine hours' heating. The acid separates from boiling water, in which it is fairly readily soluble, in fan-shaped clusters of minute needles containing one and a-half molecules of water of crystallisation. After drying at  $110^{\circ}$ , it melts and effervesces at  $239^{\circ}$  (corr.). The acid gives an immediate

red coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution.

Found, in air-dried material: loss at  $110^{\circ}$  = 12.7.

$1\frac{1}{2}\text{H}_2\text{O}$  requires 12.6 per cent.

In substance dried at  $110^{\circ}$ , C = 63.5; H = 4.5; N = 14.8.

$\text{C}_{10}\text{H}_8\text{O}_2\text{N}_2$  (188.1) requires C = 63.8; H = 4.3; N = 14.9 per cent.

*Ethyl 2-phenylglyoxaline-4-carboxylate* crystallises from ethyl acetate in minute needles, which melt at  $189^{\circ}$  (corr.), sintering above  $183^{\circ}$ . It is readily soluble in alcohol or hot ethyl acetate, less readily so in cold ethyl acetate, and very sparingly so in water. It gives no coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution.

Found, in air-dried substance: loss at  $100^{\circ}$  = 9.5.

Found, in dried substance: C = 66.5; H = 5.7; N = 12.9.

$\text{C}_{12}\text{H}_{12}\text{O}_2\text{N}_2$  (216.1) requires C = 66.6; H = 5.6; N = 13.0 per cent.

*Ethyl Glyoxaline-4-acetate*.—This was prepared previously by the action of alcoholic hydrogen chloride on 4-cyanomethylglyoxaline (T., 1911, 99, 681), and can also be obtained by the esterification of the corresponding acid or by the action of alcohol on the hydrochloride of glyoxaline-4-acetyl chloride. It gives a deep red colour when mixed with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate.

*Glyoxaline-4-acetyl chloride hydrochloride* can be prepared in a crystalline state by the method given below. The crude product contains less than the theoretical amount of chlorine, and we have been unable to devise a satisfactory method of purifying it.

Five grams of phosphorous pentachloride and 6 c.c. of thionyl chloride were heated on the water-bath to incipient ebullition (about  $50^{\circ}$ ), and 4 grams of glyoxaline-4-acetic acid hydrochloride were added, the mixture being well stirred. Evolution of hydrogen chloride took place, and the pasty mass quickly became crystalline, forming minute leaflets. When the reaction had ended, the mass was diluted with chloroform, filtered, washed with chloroform, and dried in a vacuum over sulphuric acid and sodium hydroxide. The dry, crystalline powder obtained in this way was pale pink and amounted to 4.4 grams, that is, 97.7 per cent. of the theoretical. The specimen with the highest chlorine content melted and decomposed at  $127^{\circ}$  (corr.), the others at  $125^{\circ}$ .

Found: C = 33.2; H = 3.5; Cl = 35.5, 35.1, 36.8 (in different specimens).

$\text{C}_8\text{H}_5\text{ON}_2\text{Cl}\cdot\text{HCl}$  (181.0) requires C = 33.2; H = 3.3; Cl = 39.2 per cent.



*Ethyl β-Glyoxaline-4-propionate.*—This was purified by crystallisation of the hydrogen oxalate from alcohol. The ester formed an oil, which gave an immediate blood-red colour with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate.

The *hydrogen oxalate* separates from alcohol in colourless, shimmering leaflets, which are anhydrous and melt at 160° (corr.) after sintering from 155°. It is readily soluble in water or hot alcohol, but sparingly so in cold alcohol.

Found: C=48.1; H=6.0; N=11.8.

(C<sub>8</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub>)<sub>4</sub>(C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>)<sub>3</sub> (942.7) requires C=48.4; H=5.8; N=11.9 per cent.

*Ethyl α-hydroxy-β-glyoxaline-4-propionate* crystallises from dry chloroform in minute, colourless plates which melt at 118–119° (corr.), and are anhydrous. It is readily soluble in water or alcohol, sparingly so in chloroform, and insoluble in ether. It gives a cherry-red colour with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate.

Found: C=52.3; H=6.5.

C<sub>8</sub>H<sub>12</sub>O<sub>3</sub>N<sub>2</sub> (184.1) requires C=52.2; H=6.6 per cent.

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## LXXXVIII.—*The Free Energy of Dilution of Aqueous Sodium Chloride Solutions.*

By ARTHUR JOHN ALLMAND and WILFRID GUSTAV POLACK.

THIS work, which was commenced a few months prior to the outbreak of war, was undertaken with the view of investigating systematically the relations existing between activity and concentration for the different molecular species present in aqueous solutions of typical binary electrolytes, working between the limits of saturated solutions and solutions of dilution only determined by difficulties of measurement. G. N. Lewis, to whom we owe the introduction into thermodynamics of the term "activity" (*Zeitsch. physikal. Chem.*, 1907, 61, 129), has also provided a very convenient way of expressing the deviations—true or apparent—from the laws of perfect solutions which are exhibited by the ions and by the molecules of undissociated electrolyte, namely, by the use of the magnitude "activity coefficient." The "activity coefficient" of a

chemical species in any phase is the ratio activity/concentration for that species in the given phase. In the case of electrolytes, activity can be measured by any of the related thermodynamic methods (that is, osmotic pressure, lowering of freezing point, electromotive force), whilst the concentration can be determined from conductivity methods, with or without the rather uncertain correction for viscosity. The extent to which the activity coefficient differs from unity and changes in magnitude with change of concentration is a measure of the abnormality of the thermodynamic behaviour of the chemical species in question under the experimental conditions.

The same author (*J. Amer. Chem. Soc.*, 1912, **34**, 1631), in an important critical survey of the subject, discusses the then available experimental data, including measurements of solubility product, depression of freezing point, and electromotive force. Assuming the validity of the conductivity method of arriving at concentration values, the conclusion drawn is that, whilst in very dilute solutions concentrations and activities of ions are directly proportional, their activity coefficients fall off somewhat as the solutions become more concentrated. On the other hand, the activity coefficients of the undissociated molecules of electrolytes increase rapidly with increase of concentration. Specific effects for ions would appear to enter at concentrations higher than 0.1*N*. Later in his paper, he seriously disputes the basis of the Kohlrausch method of arriving at the ionic and undissociated-molecule concentrations, believing it to be vitiated by changes in the mobility of ions with concentration, a view first put forward by Jahn (*Zeitsch. physikal. Chem.*, 1900, **33**, 545). His final conclusion is that ionic activities and concentrations are proportional in dilute solutions up to 0.1*N*, the activity coefficients therefore being unity throughout this region.

These views have been much discussed during the last few years. The conclusion generally drawn (see, for example, Bates, *J. Amer. Chem. Soc.*, 1915, **37**, 1421) is that the conductance-viscosity ratio is a measure of concentration, leaving unexplained the undoubted discrepancies between activity and concentration even in dilute solutions. When the present measurements were undertaken, however, the matter had still to be regarded as an open one. One point which it was hoped to elucidate was the magnitude of the specific effects, if any, in the variations of the activity coefficients of the ions with concentration. By making measurements with four different electrolytes, such as MA, MB, NA, and NB, and by comparing these with one another at concentrations at which the ionic concentrations in the solutions of the four different electro-

lytes, as determined by the conductance-viscosity ratio, are identical, it should be possible to test this point for the ions  $M'$ ,  $N'$ ,  $A'$ , and  $B'$ . Hitherto, the assumption—a probable one—has been made that the activities of the two ions are identical in any solution of a binary electrolyte where their concentrations, excluding complex-formation and solvation, are necessarily the same.

The electromotive force method of measurement was chosen. Tolman and Ferguson\* (*J. Amer. Chem. Soc.*, 1912, **34**, 232) had already used it successfully for measurements of activity coefficient on dilute aqueous solutions of hydrochloric acid. It was intended to use as electrolytes the chlorides, bromides, iodides, hydroxides, and sulphates of sodium, potassium, and lithium, and one of the authors had already found (T., 1914, **105**, 1941) the amalgam electrodes prepared according to the directions of G. N. Lewis and his co-workers (*J. Amer. Chem. Soc.*, 1910, **32**, 1459; 1912, **34**, 1119) to function satisfactorily.

The principle of the method is briefly as follows. If two cells are set up,

(1) Electrode reversible to ion A.	Solution of AB. Concentration $C_1$ .	Electrode reversible to ion B.
(2) Electrode reversible to ion A.	Solution of AB. Concentration $C_2$ .	Electrode reversible to ion B.

the electrode systems being identical, and the two combinations only differing in the values of the concentrations  $C_1$  and  $C_2$  ( $C_1 > C_2$ ), the difference between the electromotive forces of the two cells ( $E$ ) is a measure of the free energy of dilution of AB from the concentration  $C_1$  to the concentration  $C_2$ . If the ions are both univalent, the free energy of dilution per gram-molecule is expressed by

$$FE = RT \ln \frac{[a_1]_{\text{undiss.}}}{[a_2]_{\text{undiss.}}} = RT \ln \frac{[a_1]_A \cdot [a_1]_B}{[a_2]_A \cdot [a_2]_B},$$

where  $a$  represents activity and the suffixes refer to the two solutions and to the undissociated molecules and the different ions. Making the assumption mentioned above that  $[a]_A = [a]_B$  for the same solution, we have

$$FE = 2RT \ln \frac{[a_1]_{\text{ion}}}{[a_2]_{\text{ion}}}.$$

The measurements of electromotive force allow, therefore, the immediate calculation of activity ratios for the solutions concerned, and from these, using concentration data obtained from measure-

\* Professor G. N. Lewis informed us by letter that Professor Tolman had no intention of continuing the work further.

ments of conductivity, the activity coefficient ratios follow immediately.

In order to calculate heats of dilution, measurements were carried out at 18° and 25°. Their close proximity was compensated for by the possibility of utilising the existing conductivity data for calculations of concentration.

Measurements with sodium chloride were completed before the end of 1914. It has been impossible to resume the work, and the results are consequently published as they stand.

Several papers dealing with the same or with closely related problems have been published in America in the interval. Such are those of Bates (*loc. cit.*), MacInnes and Parker (*J. Amer. Chem. Soc.*, 1915, **37**, 1445), Forbes and Anderegg (*ibid.*, 1676), Harned (*ibid.*, 2460; 1916, **38**, 1986; 1918, **40**, 1461), Ellis (*ibid.*, 1916, **38**, 787), Ferguson (*J. Physical Chem.*, 1916, **20**, 326), Linhart (*J. Amer. Chem. Soc.*, 1917, **39**, 615, 2601), Noyes and Ellis (*ibid.*, 2532), Pearce and Mortimer (*ibid.*, 1918, **40**, 509), and Rodebush (*ibid.*, 1204). Some of these will be referred to later.

#### EXPERIMENTAL.

The sodium amalgam was prepared precisely as described by Lewis and Kraus (*loc. cit.*), except that the mercury was distilled over more rapidly on to the sodium by enclosing the containing vessel in an asbestos oven, the mercury being heated to about 280° and the sodium to 130°. The mercury employed, both for making the amalgams, as also for the calomel electrodes, was purified by passing at least twice down the usual column of acid mercurous nitrate. The amalgam was indistinguishable from mercury in appearance, and remained so for more than four years.

The amalgam electrode vessels were as designed by Lewis and Kraus. The calomel electrode vessels used were chiefly (see, however, later) of the usual Ostwald type, the connecting tubes being made as short and as wide as practicable in order to diminish the resistance. The calomel, after being washed several times by shaking with a small quantity of the solution and a little mercury, was shaken with a larger quantity of the solution, the liquid with the calomel in suspension being drawn into the carefully cleaned and dried electrode vessels. From four to six electrodes were prepared for each concentration of sodium chloride solution for which the electromotive force was measured, and, after allowing time for their potentials to become constant (usually eighteen hours), they were compared against one another. Electrodes which agreed at 18° were always found to agree at 25°. When several electrodes

had been obtained showing a maximum difference between any pair of about 0.3 millivolt, one of them was chosen for the actual measurements (or one for the measurements at 18° and another for 25°), and generally compared again with the others after the measurements.

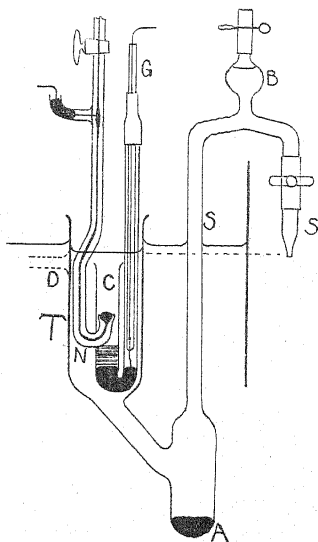
In all, seven concentrations of sodium chloride were employed, namely, 5.41*N* (saturated at 18°),\* 3*N*, *N*, 0.5*N*, 0.1*N*, 0.02*N*, and 0.01*N*. The solutions were made up to volume at 18°. With solutions of concentration 0.5*N* and above, the measurements can readily be carried out with considerable accuracy. The solution is contained in a glass tube 10 cm. long and 3.5 cm. in diameter, suitably clamped in the thermostat, and into this tube dip the nozzles of the amalgam and calomel electrodes, also clamped to separate stands. The essential parts of the calomel electrode are also in the thermostat. While the measurement is being made, amalgam drops very slowly from the nozzle of the electrode, and the electromotive force remains practically constant.

With the more dilute solutions, however, several difficulties arise. The most serious of them is the decomposition of the amalgam on coming into contact with the solution. As pointed out by Lewis and Kraus, the decomposition takes place chiefly on small specks floating on the surface of the amalgam, and when the electrode has been in use for a minute or so, these are carried away. Nevertheless, the amalgam which collects at the foot of the tube containing the solution continues to decompose, and there is always some visible decomposition at the nozzle of the electrode, even when the surface seems to be perfectly clean. This tends to make the potential of the electrode less negative in two ways, namely, (i) by increasing the sodion concentration in the liquid surrounding the nozzle of the electrode, and (ii) by decreasing the sodium concentration in the surface layers of the amalgam. The effect of (i) obviously increases rapidly with increasing dilution, not only because of the increase in the actual rate of decomposition, but also because of the relatively larger effect produced on the concentration of the sodions. The consequence of (ii) is that the potential fluctuates, rising suddenly as each drop of amalgam becomes detached, exposing a fresh surface. To counteract this, it is necessary to allow the amalgam to flow more rapidly from the electrode, and this means still more decomposition in the liquid. In consequence of these facts, it was found necessary for the measurements with dilute solutions to use an apparatus of the type shown in Fig. 1, in which the product of decomposition is

\* This solution was actually made up to saturation, and its concentration calculated from the available data, not experimentally determined.

prevented from accumulating round the electrode. In its first form, solution flowed from a large dropping funnel into the tube *T*, and up through the siphon tube *S*. The amalgam dropping from the electrode *N* collected at *A*, the alkali formed by the decomposition being thus carried away from the electrode, which was always surrounded by fresh solution. Hydrogen produced at *A* collected at *B*. *C* is the calomel electrode described below.

FIG. 1.



Later, the apparatus was modified so that the solution did not flow directly into the tube *T*, but passed first through a close-wound spiral of thin-walled tubing immersed in the thermostat and sealed into the tube *T* at *D*. With the 0.01*N*-solution, the flow of electrolyte at the moment of measurement must be fairly rapid, and this precaution becomes essential to ensure that the temperature of the solution is accurately that of the thermostat.

Another difficulty which arises with the more dilute solutions is

the comparatively high resistance of the ordinary type of calomel electrode. For the 0.01*N*-measurements, the form shown in Fig. 1 was employed. *C* is the electrode vessel proper, contact being made with the mercury by means of a platinum wire sealed into the end of a narrow glass tube, *G*. When the electrode was not actually in use, the mouth of the tube *C* was closed by a cork, a little of the liquid being removed by a pipette, care being taken not to disturb the calomel at the foot of the tube. These electrodes had a much lower resistance than the others, but were less trustworthy. Several were made up for preliminary tests, and in one or two instances considerable variations occurred, probably due to mechanical disturbances. With suitable precautions, however, they proved satisfactory enough.

In the present investigation, it appeared that the limit of dilution was reached at 0.01*N*, owing to the decomposition of the amalgam. Much greater disturbances occurred between individual readings than in any of the other cases. The electromotive force tended to increase with increasing rate of flow of the electrolyte,\* even until the latter reached the maximum possible with the apparatus used, so that the effect of decomposition was apparently never quite eliminated. The figures given for this dilution are therefore less trustworthy than any of the others. One would expect these to be, if anything, too low. The values obtained by extrapolation would also appear to indicate this. They are probably more trustworthy than the experimental values, and are used instead of these in subsequent calculations.

The electromotive forces were measured with a Clark-Fisher potentiometer and cadmium cell, both of which had been tested at the National Physical Laboratory. The potentiometer could be read to 0.0001 volt as long as the resistance in the circuit was not excessively high. Potentiometer, galvanometer, cells, etc., and also the stands to which the electrodes were clamped, were all carefully insulated on glass.

In all, three different amalgams were prepared, each being contained in a pair of electrodes. In each measurement several readings were taken with each electrode with various rates of flow of the amalgam, and, where the special apparatus was used (0.1*N* and more dilute solutions), with various rates of flow of electrolyte. The difference between the values obtained for the two electrodes was in every case less than the possible experimental errors due to other sources. The figures given represent in each

\* Incidentally this shows that the flowing electrolyte had reached the temperature of the bath, as the electromotive force increases with rise of temperature.

case the mean of the various individual readings with the two electrodes (in some cases of two or more complete sets of such readings), together with the maximum error likely to be involved, taking into account the variations in the individual readings in the calomel electrodes themselves, etc.

The three pairs of electrodes contained amalgams with the following respective percentages of sodium:

(a) 0.2234; (b) 0.1657; (c) 0.1389.

These values were determined by weighing out small quantities of the amalgam, acidifying, and, on completion of the decomposition, estimating the excess of acid by titration.

The electrodes (a) contained only a small quantity of amalgam, and were only used for two dilutions, namely, 0.1*N* and 0.02*N*. As the measurements were carried out with stationary electrolyte and not with the special apparatus, there was a fair amount of decomposition. The values must therefore be regarded as more or less preliminary. Nevertheless, there is good agreement between the values for the difference of electromotive force at 0.1*N* and 0.02*N* furnished by the two pairs of electrodes (a) and (b), the special apparatus being used in the case of (b).

Tables I and II give the actually measured electromotive forces in volts at 18° and 25° for the three amalgams (a), (b), and (c).

TABLE I.

18°.			
Concentration.	(a)	(b)	(c)
5.41 <i>N</i> .....	—	—	2.0281 ± 0.0002
3 <i>N</i> .....	—	—	2.0770 ± 0.0001
1 <i>N</i> .....	—	2.1466 ± 0.0002	2.1398 ± 0.0002
0.5 <i>N</i> .....	—	2.1792 ± 0.0003	—
0.1 <i>N</i> .....	2.2635 ± 0.0010	2.2534 ± 0.0004	—
0.02 <i>N</i> .....	2.3384 ± 0.0010	2.3274 ± 0.0005	—
0.01 <i>N</i> .....	—	—	2.350 ± 0.002

TABLE II.

25°.			
Concentration.	(a)	(b)	(c)
5.41 <i>N</i> .....	—	—	2.0283 ± 0.0001
3 <i>N</i> .....	—	—	2.0784 ± 0.0001
1 <i>N</i> .....	—	2.1499 ± 0.0002	2.1430 ± 0.0002
0.5 <i>N</i> .....	—	2.1838 ± 0.0003	—
0.1 <i>N</i> .....	2.2710 ± 0.0010	2.2596 ± 0.0003	—
0.02 <i>N</i> .....	2.3450 ± 0.0010	2.3336 ± 0.0010	—
0.01 <i>N</i> .....	—	—	2.358 ± 0.002

Assuming that the difference in potential between amalgams (b) and (c) as deduced from the readings with *N*-solutions is 0.0068



volt at 18° and 0.0069 volt at 25°, the values which the electromotive forces would have for amalgam (c) and 0.5*N*-, 0.1*N*-, and 0.02*N*-solutions can be calculated. They are contained in table III and are plotted in Fig. 2. In view of what has already been said (see p. 1026), the figures for 0.01*N*-solutions given in the table are not the experimental values, but those extrapolated from the curve.

FIG. 2.

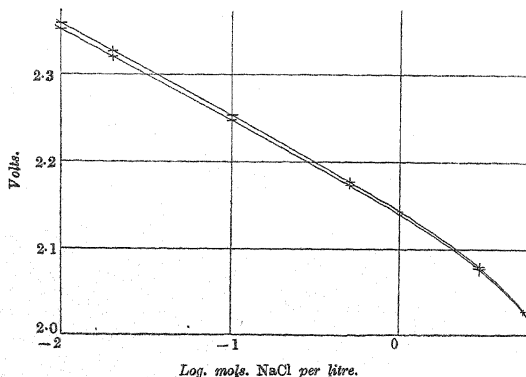


TABLE III.

		E.M.F. for the combination Hg   Hg <sub>2</sub> Cl <sub>2</sub> aqueous NaCl   0.1389 per cent. sodium amalgam.		$\alpha$ (defined by $e_t = e_{18}[1 + (t - 18)\alpha]$ )
<i>C</i> in mols. NaCl per litre.	<i>C</i> in mols. NaCl per 1000 grams of water.	18°. Volts.	25°. Volts.	
5.41	6.12	2.0281	2.0283	$141 \times 10^{-7}$
3.0	3.196	2.0770	2.0784	963
1.0	1.022	2.1398	2.1430	2140
0.5	0.5034	2.1724	2.1769	2960
0.1	0.1003	2.2466	2.2527	3880
0.02	0.02003	2.3206	2.3267	3760
0.01	0.01001	2.3520	2.3585	3950
		( $\pm 0.0005$ )	( $\pm 0.0005$ )	

*Free and Total Energy Changes of Cell Reaction.*

Taking the Faraday as 96,540 coulombs, the decreases in free and total energy of the system per gram-equivalent transformed can be calculated for the cell reaction

$2\text{Na}$  (in form of 0.1389 per cent. amalgam) +  $\text{Hg}_2\text{Cl}_2 \rightarrow$   
 $2\text{Hg} + 2\text{NaCl}$  (in aqueous solution)

from the figures in table III. The results are contained in table IV.

TABLE IV.

C in mols. NaCl per 1000 grams of water.	Free energy decrease at		Total energy decrease at 18°. Joules.
	18°. Joules.	25°. Joules.	
6.12	195795	195815	195000
3.196	200520	200650	195030
1.022	206575	206885	193690
0.5034	209725	210160	191600
0.1003	216885	217475	192360
0.02003	224030	224620	199500
0.01001	227060	227695	200790

The figures indicate that the decrease of total energy, or heat effect of the reaction, at first falls off as the electrolyte becomes more dilute, and then commences to increase. The results are plotted in Fig. 3, and it will be seen that the curve has a minimum at about 0.25—0.3 molecule of sodium chloride per 1000 grams of water. Too much stress, however, is not laid on this result, or on certain other calculations of heat effects recorded subsequently in this paper. The range of temperature over which measurements were made is small, and the calculations are correspondingly affected, whilst for the more dilute solutions the possible errors in the measurements must be seriously taken into account.

*Sodium Chloride Concentration Cells without Transference.*

By subtracting the values of electromotive force given in table III from the corresponding values for the 0.1*N*-solution, figures are obtained for the electromotive forces of sodium chloride concentration cells "without transference," one of the two solutions in every case being 0.1*N* (p. 1022). These values are contained in table V.

TABLE V.

C in mols. NaCl per 1000 grams of water.		E.M.F. at		$\alpha$ (defined by $e_s$ . $=e_{18}[1+(t-18)\alpha]$ ).
$C_1$ .	$C_2$ .	18°. Volts.	25°. Volts.	
6.12	0.1003	0.2185	0.2244	$386 \times 10^{-5}$
3.196	"	0.1696	0.1743	396
1.022	"	0.1068	0.1097	388
0.5034	"	0.0742	0.0758	308
0.02003	"	-0.0740	-0.0740	0
0.01001	"	-0.1054	-0.1058	54

We can compare these figures with those obtained by other investigators for similar cells. Thus, whilst for  $\frac{C_1}{C_0} = \frac{0.1}{0.01}$  (normal concentrations) sodium chloride gives a figure of 0.1058 volt at 25°, other experimenters have obtained the following figures for hydrochloric acid and for potassium and lithium chlorides:

FIG. 3.

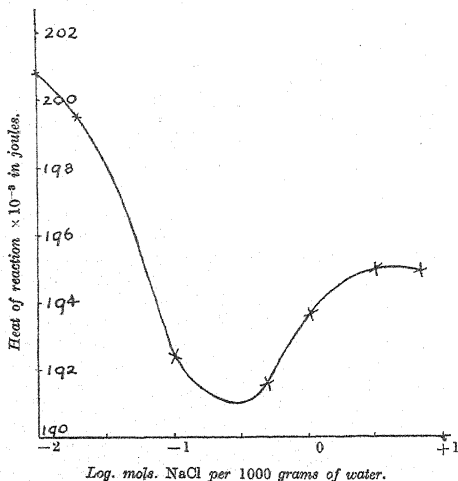


TABLE VI.

Electrolyte.	Volt.	Observer.
HCl	0.114	Noyes and Ellis ( <i>loc. cit.</i> )
KCl	0.1089	MacInnes and Parker ( <i>loc. cit.</i> )
LiCl	0.10433	Pearce and Mortimer ( <i>loc. cit.</i> )

By a comparison of the figures for such cells with those given by the corresponding cells with transference, the transport number of the electrolyte can be calculated. The electromotive force of the cell without transference (p. 1022) is  $e_1 = 2\frac{RT}{F} \ln \frac{a_1}{a_2}$ , whilst that of the cell with transference is  $e_2 = 2N\frac{RT}{F} \ln \frac{a_1}{a_2}$ , where  $N$  is the

cation transport number if electrodes reversible to the anion are employed. Consequently,

$$N_c = \frac{e_2}{e_1}$$

Measurements of sodium chloride concentration cells with transference were carried out at 18° by Jahn (*Zeitsch. physikal. Chem.*, 1902, 41, 298), using calomel electrodes and dilute solutions of electrolyte. Table VII contains figures taken from his paper, together with corresponding values drawn from table V or Fig. 2. In the last column are the calculated transport numbers for the sodium ion.

TABLE VII.

$C_1$ in mols. per litre.	$C_2$ in mols. per litre.	$e_1$ .	$e_2$ .	$N_c$ .
0.02	0.01	0.0314	0.01293	0.412
0.04	0.02	0.0317	0.01268	0.400
0.06	0.03	0.0318	0.01255	0.394

Experimental determinations gave the following results (Abegg, "Handbuch," II, i, 231):

$C$ .	$t^\circ$ .	$N_c$ .	Observer.
3—5N.	10°	0.352	Hittorf.
0.7N.	16	0.366	"
0.005N.	10	0.379	"
1/30—1/150N.	0	0.387	Jahn-Schulz.
1/8—1/14N.	18	0.395	"
1/8—1/150N.	30	0.404	"

In a way exactly similar to that by which the figures in table V were obtained from the data of table III, we can calculate from table IV values for the decrease in total energy (heat content) and free energy associated with the transfer of one molecule of sodium chloride from any concentration given in the table to a 0.1 molar normal solution. Table VIII contains the results.

TABLE VIII.

$C$ in mols. NaCl per 1000 grams of water.		Free energy decrease in joules at		Total energy decrease in joules at
$C_1$ .	$C_2$ .	18°.	25°.	18°.
6.12	0.1003	21090	21660	-2640
3.196	"	16365	16825	-2670
1.022	"	10310	10590	-1330
0.5034	"	7160	7315	+760
0.02003	"	-7145	-7145	-7145
0.01001	"	-10175	-10220	-8430

In table IX, the results in the last column of table VIII are expressed as the total energy decrease attending the transfer of

one molecule of sodium chloride from a concentration of 6.12 molecules per 1000 grams of water to other concentrations given in the first column.

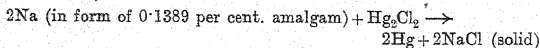
TABLE IX.

C in mols. NaCl per 1000 grams of water.	Heat effect at 18°.	
	Joules.	Calories.
6.12	—	—
3.196	+30	+7
1.022	-1310	-313
0.5034	-3400	-812
0.1003	-2640	-630
0.02003	+4505	+1075
0.01001	+5790	+1382

The curve representing the variation of the heat effects of tables VIII and IX with concentration of electrolyte will, of course, be exactly similar in form to that in Fig. 3. The magnitude of the possible errors involved must again be emphasised. This point is also brought out by the last column in table V. It is improbable that the value of  $\alpha$ , after approximating to the "ideal" figure of  $366.5 \times 10^{-5}$  in concentrated solutions, should fall and fluctuate in the dilute solutions, as the experimental figures appear to indicate.

The free energies of dilution of sodium chloride at 25° from saturated solution to 1.0*N* and from 1.0*N* to 0.1*N* have been calculated by Rodebush (*loc. cit.*) from freezing-point measurements to be respectively 2477 and 2464 calories.

Our value for  $-\Delta F_{298}$  from 1.0*N* to 0.1*N* can be obtained from column four of table VIII, and is  $10590/4.189 = 2528$  cals., a rather higher figure. A saturated solution of sodium chloride at 25° is 5.43*N*, and contains 6.14 molecules per 1000 grams of water (as against 5.41*N* and 6.12 molecules per 1000 grams at 18°). If we extrapolate to this concentration on Fig. 2, we obtain the value 2.0279 for the electromotive force in volts of the experimental cell at 25°. From this figure and that for the cell with saturated solution at 18°, we calculate for the reaction

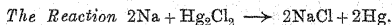


that  $-\Delta F_{298}$  is 195,775 joules and  $-\Delta H_{291}$  is 196,585 joules, in both cases for the transformation of 1 gram-equivalent. From this value of  $-\Delta F_{298}$  and from  $-\Delta F_{298}$  for a 1.0*N*-solution (table IV, column three), we calculate that  $-\Delta F_{298}$  from saturated solution to 1.0*N* is  $11,110/4.189 = 2652$  calories, a much higher figure than that of Rodebush.

The difference of the above value of  $-\Delta H_{291}$  for the reaction

involving the production of solid sodium chloride and that of  $-\Delta H_{291}$  for the reaction involving the production of saturated sodium chloride solution (see table IV) furnishes us with the heat of solution of one molecule of sodium chloride in a saturated solution at  $18^\circ$ . This value comes to 195,000—196,585 joules, or -378 calories. There are no experimental determinations with which this figure can be directly compared. Using the van't Hoff isochore, and taking the solubility of sodium chloride as 35.79 grams and 35.92 grams per 100 grams of water at  $18^\circ$  and  $25^\circ$  respectively, we calculate the heat of solution as -89.5 calories, a far smaller value. The assumption of the validity of the gas laws, however, involved in this equation is certainly not justified, and we believe our value to be nearer the truth.

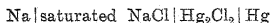
If we compare the values deduced from our curve for heats of solution in given quantities of water and for heats of dilution with experimental values, the concordance is only moderate. For the heat of solution of one molecule of sodium chloride in 9.2 molecules of water, Stackelberg (Landolt-Börnstein, "Tabellen," 4th edition, p. 875) found -410 calories; for the same in 10 molecules of water, van Deventer and van de Staat (*Zeitsch. physikal. Chem.*, 1892, 9, 55) found -475 calories. We deduce, respectively, -371 and -373 calories. For the heat of solution of one gram-molecule of sodium chloride in 100 gram-molecules of water, Thomsen (Landolt-Börnstein, "Tabellen," 4th edition, p. 875), Stackelberg (*Zeitsch. physikal. Chem.*, 1898, 26, 545), and van Deventer and van de Staat found, respectively, -1180 calories, -1030 calories, and -1130 calories. Our value is -1110 calories. When, however, we compare the different values for heats of dilution over concentration limits included in this range, the discrepancies are large. We get much smaller heat effects for dilution up to concentrations of one molecule of sodium chloride to 20 molecules of water, and much larger for dilutions between  $1\text{NaCl}:50\text{H}_2\text{O}$  and  $1\text{NaCl}:100\text{H}_2\text{O}$ . Thus van Deventer and van de Staat found the molar heat of dilution from  $1\text{NaCl}:10\text{H}_2\text{O}$  to  $1\text{NaCl}:20\text{H}_2\text{O}$  to be -247 calories, whereas our figure is -17 calories. Similarly, their value for dilution from  $1\text{NaCl}:50\text{H}_2\text{O}$  to  $1\text{NaCl}:100\text{H}_2\text{O}$  is -128 calories per mol. NaCl. Our value is -463 calories.



Lewis and Kraus (*loc. cit.*) found that 0.2062 per cent. amalgam at  $25^\circ$  is 0.8456 volt positive to metallic sodium, whilst the temperature-coefficient of the electromotive force of the combina-

tion is  $-0.0000408$  volt/degree. It follows that the amalgam is  $0.8459$  volt positive to sodium at  $18^\circ$ .

The measurements in tables I and II show that our amalgam (*a*) is  $0.0068$  volt positive to (*b*) at  $18^\circ$ , and that (*b*) is  $0.0110$  volt positive to (*a*). At  $25^\circ$ , the potential differences are  $0.0069$  and  $0.0114$  volt respectively. Plotting these figures and interpolating to find the relative potentials of the  $0.2062$  per cent. amalgam at these two temperatures, we obtain the result that it is negative to the amalgam (*c*) ( $0.1389$  per cent.) by  $0.01465$  volt at  $18^\circ$  and  $0.01495$  volt at  $25^\circ$ . Combining these values with the figures of Lewis and Kraus, it follows that amalgam (*c*) is positive to sodium by  $0.86055$  volt at both  $18^\circ$  and  $25^\circ$ . From the electromotive forces of the cells, amalgam (*c*) | saturated NaCl |  $\text{Hg}_2\text{Cl}_2$  | Hg, experimentally determined for  $18^\circ$  and extrapolated for  $25^\circ$ , we calculate for the cell

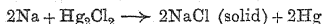


that

$$e_{291} = 2.88865 \text{ volts,}$$

$$e_{298} = 2.88845 \quad , ,$$

and for the cell reaction



that

$$-\Delta F_{291} = 66,573 \text{ calories}$$

$$-\Delta F_{298} = 66,569 \quad , ,$$

$$-\Delta H_{291} = 66,740 \quad , ,$$

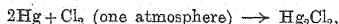
per gram-equivalent transformed. The "calorimetric" value of  $-\Delta H_{291}$  is obtained by subtracting the accepted heat of formation of  $\frac{1}{2}\text{Hg}_2\text{Cl}_2$  (Varet) from the heat of formation of NaCl (Thomsen), that is,  $31,315$  from  $97,700$ , leading to a figure of  $66,385$  cals.

#### *Free Energy in Solution of One Molecule of Sodium Chloride.*

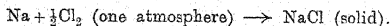
By adding to the above values of  $-\Delta F$  for the reaction



the values of  $-\Delta F$  for the reaction



that is,  $25,255$  and  $25,125$  cals. per gram-equivalent at  $18^\circ$  and  $25^\circ$  respectively (Ellis, *loc. cit.*, p. 757), we arrive at once at values for the difference in free energy between sodium and chlorine on the one hand and solid sodium chloride on the other, namely, for the reaction



$$-\Delta F_{291} = 91,828 \text{ calories,}$$

$$-\Delta F_{298} = 91,694 \quad , ,$$

As a check on these values, we can calculate  $-\Delta H_{291}$ . The value found is 97,400 cals., whilst the calorimetric value already referred to above is 97,700 cals.

We are now in a position to state the values of the free energy of one molecule of sodium chloride at different dilutions in aqueous solution, taking the free energies of the two elements concerned, sodium and chlorine, as zero. The figures are contained in table X, and are obtained by combining the above values for the free energy of solid sodium chloride with the figures in table VIII and the value deduced on p. 1032 for  $-\Delta F_{298}$  from saturated to 1.0*N*-sodium chloride. Similar figures for the total energy of a molecule of sodium chloride could also be calculated, but the data are not regarded as sufficiently trustworthy.

TABLE X.

Free energy of 1 mol. of NaCl in calories at

<i>C</i> in mols. per litre (saturated).	18°.		25°.	
3.0	-91828		-91694	
1.0	-92956		-92858	
0.5	-94401		-94346	
0.1	-95154		-95128	
0.02	-96863		-96874	
0.01	-98568		-98580	
	-99292		-99314	

*Activities of Ions and Undissociated Molecules.*

From the data contained in table V, activity ratios can be calculated by the method given on p. 1022. This has been done, and the results are contained in table XI.

TABLE XI.

<i>C</i> in mols. per 1000 grams of water.	Activity NaCl <sub>0</sub>		Activity Na <sup>+</sup>		Activity of Na <sup>+</sup> (assuming value in 0.1003 solu- tion is 0.073 at 25°).	Thermo- dynamic degree of dissocia- tion.
	Activity NaCl <sub>0.1003</sub>		Activity Na <sub>0.1003</sub> <sup>+</sup>			
	18°.	25°.	18°.	25°.		
6.12	6096.0	6249.0	78.1	79.05	5.771	0.94
3.196	867.0	874.4	29.44	29.57	2.159	0.67
1.022	70.8	71.7	8.414	8.468	0.618	0.60
0.5034	19.20	19.15	4.392	4.376	0.319	0.63
[0.1003	1.0	1.0	1.0	1.0	0.073	0.73]
0.02003	0.0522	0.0560	0.229	0.237	0.0173	0.86
0.01001	0.0149	0.0162	0.122	0.127	0.0093	0.93

From the ratios in columns two to five, and assuming with Harned (*J. Amer. Chem. Soc.*, 1918, 40, 1461) that the most



likely value for the ionic activity of such an electrolyte as sodium chloride in 0.1*N*-solution is 0.073, the values in columns six and seven are calculated. The term "thermodynamic degree of dissociation" to denote the ratio of ionic activity to total concentration seems preferable to "activity coefficient," as used by Ellis (*loc. cit.*). The latter term should be retained for expressing the ratio activity/concentration for the same molecular species, according to the nomenclature introduced by Lewis.

This table shows that the thermodynamic degree of dissociation first falls off as the concentration of the dissolved sodium chloride increases from 0.01*N*, passes through a minimum value at about 1*N*, and then increases to the high figure of 0.94 at the saturation point. This behaviour is shared qualitatively by aqueous hydrogen chloride and potassium chloride solutions. The former show a marked minimum for the value of the thermodynamic degree of dissociation at about 0.5*N* (Ellis, *loc. cit.*), whilst for potassium chloride solutions the lowest value lies at about 2*N* (Harned, *J. Amer. Chem. Soc.*, 1916, **38**, 1986).

Lithium chloride solutions have not yet been investigated over a sufficient range to discover a minimum, supposing one to exist.

Our values for this function can be compared with those obtained by Harned (*J. Amer. Chem. Soc.*, 1918, **40**, 1461) from measurements of sodium chloride concentration cells with transference. His figures are given in table XII, and the agreement with ours is seen to be good.

TABLE XII.

<i>C</i> of NaCl in mols. per litre.	Activity. <i>T</i> = 25°.	Thermodynamic degree of dissociation.
3.0	2.261	0.754
2.0	1.397	0.698
1.0	0.628	0.628
0.5	0.312	0.624
0.3	0.192	0.64
[0.1	0.073	0.73]

The value of 0.0093 for the activity of the sodium ion in 0.01*N*-solution, obtained on the assumption that the activity in 0.1*N*-solution is 0.073, is identical with that assumed by Linhart (*J. Amer. Chem. Soc.*, 1917, **39**, 2601) for the activity of the potassium and hydrogen ions in 0.01*N*-solutions. His assumption leads to ionic activities for these ions in 0.1*N*-solutions of 0.078 and 0.082 respectively, figures considerably higher than the corresponding one for the sodium ion. If, however, we calculate the activity of the lithium ion in 0.1*N*-solution from the results of

Pearce and Mortimer (*loc. cit.*), assuming that the activity in 0.01*N*-solution is 0.0093, we arrive at a figure of 0.070, still lower than that for sodium ions. The fact that the relative degrees of hydration of the four ions in question arrange themselves in the inverse order of magnitude to that of the activities in 0.1*N*-solution may be of significance.

Owing to the present lack of suitable viscosity data to apply to the existing conductivity measurements, no attempt can be made to calculate accurately the activity coefficients of the ions and undissociated molecules. It is, however, certain that, starting from dilute solutions,  $a/c$  for the ions at first decreases, passes through a minimum, and then increases, whilst  $a/c$  for the undissociated molecules increases throughout, and reaches very high values in concentrated solutions. Sodium chloride in this respect acts in a similar way to other electrolytes.

The different points of view from which the anomalies of strong electrolytes can at present most fruitfully be discussed are dealt with in the excellent papers of Bates, Pearce and Mortimer, Harned and others, already referred to, and there is no need to add anything here, particularly as there are still many gaps in absolutely necessary data unfilled.

#### *Molecular Condition of Sodium in Sodium Amalgams.*

Our experiments furnish an interesting confirmation of the work of Ramsay (T., 1889, 55, 533) and of Cady (*J. Physical Chem.*, 1898, 2, 551), who found by vapour pressure and electro-metric experiments, respectively, that sodium, dissolved in mercury at concentrations varying from 0.03 to 0.66 per cent., behaved as if it were giving an abnormally large number of osmotically active particles, that is, as if simple atoms were dissociated into something simpler. From table II, it will be seen that the electromotive forces between amalgams (*a*) and (*b*), if measured in a sodium chloride solution at 25°, would amount to 0.0114 volt, and between (*b*) and (*c*) to 0.0069 volt. Substituting these values and those for the concentrations of the amalgams in the equation

$$e = \frac{2.303 RT}{F} \frac{1}{x} \cdot \log \frac{c_1}{c_2}$$

where  $x$  represents the association factor of the metal atoms dissolved in the mercury, we find for the combination amalgam (*a*)-amalgam (*b*) that  $x$  is 0.68, and for the combination amalgam (*b*)-amalgam (*c*) that  $x$  is 0.65. These values for  $x$  correspond with apparent molecular weights of 15.6 and 15.0 respectively. Ramsay,

working at high temperatures, found that the apparent molecular weight decreased as the concentration of sodium increased. For concentrations closely corresponding with ours, values of about 18 were obtained. Cady, working at 19—20°, and measuring amalgam concentration cells, using pyridine solutions as electrolytes, obtained figures from 11.3 to 16.3, again decreasing with increasing concentration of amalgam.

At first sight, it would seem possible that sodium atoms dissolved in mercury are dissociated into sodium ions and free electrons (the latter surrounded by a condensed atmosphere of mercury molecules), and that the electrical conductivity of sodium amalgams is partly electrolytic in nature. Such a state of affairs would be analogous to that shown by Kraus (*J. Amer. Chem. Soc.*, 1908, **30**, 1323) to exist in solutions of sodium in liquid ammonia. Skaupy (*Zeitsch. physikal. Chem.*, 1907, **58**, 560), indeed, has tried to prove that the supposed equilibrium



in dilute amalgams obeys the Ostwald dilution law. The experiments of Lewis, Adams, and Lanman (*J. Amer. Chem. Soc.*, 1915, **37**, 2656) are, however, completely against this assumption. They showed that, when a current passes through a sodium amalgam solution, the sodium concentrates at the positive pole. Their suggested explanation is rendered less probable by subsequent very exact experiments by Hine (*ibid.*, 1917, **39**, 882) on the conductivity of dilute alkali metal amalgams, but it is at all events clear that the dissolved sodium is not associated with a surplus positive electric charge.

The true explanation of the apparent low molecular weights is in all probability the formation of compounds between the sodium and the mercury. The importance of taking this into account was first pointed out by Haber (*Zeitsch. physikal. Chem.*, 1902, **41**, 399). Sodium and mercury can combine to form the well-defined compound NaHg<sub>2</sub>. Abegg ("Handbuch," II, i, 679) has shown that it is a likely assumption that the concentration of free mercury in the amalgams is thereby lowered to a sufficient extent to explain Ramsay's (and also the electrometric) results. Cady (*loc. cit.*) has further demonstrated that the abnormalities in the electrometric results disappear if the heat of dilution of the amalgams is taken into account. Actually measuring this for sodium amalgam between certain concentrations, he obtained very exact agreement. Low apparent molecular weights are associated with abnormally high electromotive forces for concentration cells, with positive heats of dilution, and with the formation of exothermic compounds.

Those interested are referred to papers by Richards and Garrod-Thomas (*Zeitsch. physikal. Chem.*, 1910, **72**, 165), and by Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 501), where the situation is clearly set out.

The temperature-coefficients of our own cells were measured over too small a range to allow of the calculation from them of the heats of dilution of the sodium amalgams used.

### *Summary.*

- (1) Measurements of cells of the type

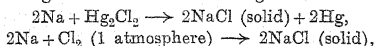
$\text{Hg}|\text{Hg}_2\text{Cl}_2$  aqueous  $\text{NaCl}$  solutions|sodium amalgam  
have been carried out at  $18^\circ$  and  $25^\circ$  for concentrations of sodium chloride ranging between  $0.01N$  and saturated solution.

(2) From these have been calculated the free and total energies of dilution of sodium chloride between the concentration limits referred to.

(3) The transport number of the sodium ion in different dilute sodium chloride solutions has been calculated.

(4) The molecular heat of solution of sodium chloride in saturated solution at  $18^\circ$  has been calculated.

- (5) The changes in free and total energies of the reactions



have been calculated.

(6) The free energies of one molecule of sodium chloride in aqueous solution at various concentrations at  $18^\circ$  and  $25^\circ$ , referred to the free energies of the elements sodium and chlorine as zero, have been calculated.

(7) The "thermodynamic degrees of dissociation" of sodium chloride in aqueous solution at different concentrations at  $25^\circ$  have been calculated, together with the corresponding activities of the sodium ion.

(8) Confirmation has been obtained of previous work on the molecular condition of sodium in sodium amalgams.

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[Received, May 31st, 1919.]

LXXXIX.—*The Active Substance in the Iodination of Phenols.*

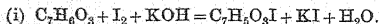
By VICTOR COFMAN.

NUMEROUS methods are known for the preparation of iodophenols, and the entrance of iodine in the molecule has been accounted for in various ways. The object of this communication is to prove that hypiodous acid is solely responsible for the iodination in a number of processes investigated, and to show that the presence of the above-mentioned substance as an intermediate compound satisfactorily explains the formation of iodophenols by the various known methods.

That hypiodous acid has the property of reacting with phenols, producing iodo-substituted compounds, is no new discovery. Selivanov (*Ber.*, 1894, **27**, 1012) pointed out that the iodination of phenol by means of nitrogen iodide is due to the hydrolysis of the latter compound and the consequent production of hypiodous acid; various other authors (Bray, *Zeitsch. physikal. Chem.*, 1906, **54**, 563; Cohn and Schultz, *Ber.*, 1905, **38**, 3294; Gardner and Hodgson, T., 1909, **96**, 1822) have suggested that the same compound may be responsible for the formation of iodophenols by the "iodine and alkali" methods, but no definite proofs have been adduced in support of this view, nor has it yet been attempted to ascribe the production of iodophenols in all the known instances to the presence of one and the same substance in the various reacting mixtures.

The earliest mention of any iodophenol is that made by Piria (*Compt. rend.*, 1843, **18**, 187), but the merit of a first investigation of this class of compounds rests with Lautemann (*Annalen*, 1861, **120**, 299), who prepared several iodophenols and iodo-salicylic acids. From his method of preparation, Lautemann inferred that, on heating iodine with salicylic acid, a direct substitution takes place, although he could not explain what happened to the displaced hydrogen.

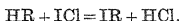
Later, Kekulé (*Annalen*, 1864, **131**, 221) showed that the compounds obtained by Lautemann's process were formed only when the mixture of iodine and salicylic acid was dissolved in alkalis. He prepared the same compounds by the action of iodine and iodic acid on salicylic acid, and explained their formation thus:



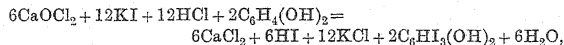
Kekulé's opinion was that iodine has the property of displacing the hydrogen atoms of certain organic compounds in the presence of a third substance capable of oxidising, or removing in some other fashion, the hydriodic acid formed during the reaction. This explanation has since been put forward to account for the formation of iodophenols by other methods, namely, (i) the "iodine and mercuric oxide" method (*Ber.*, 1872, **5**, 380); (ii) the "iodine and sodium phosphate" method (*J. Pharm. Chim.*, 1902, [vi], **15**, 217); (iii) the iodine monochloride method (*ibid.*).

According to this view, in every one of the above cases, the first part of the reaction is  $\text{HR} + \text{I}_2 = \text{IR} + \text{HI}$  (where R=phenolic radicle), and the second part consists in the removal of the hydriodic acid thus formed by the third substance present.

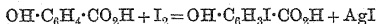
The production of iodo-substituted compounds by means of iodine monochloride was originally given a similarly simple interpretation (Brown, *Phil. Mag.*, 1854, [iv], **8**, 201):



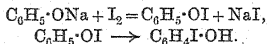
A more complicated equation was put forward by Dagener (*J. pr. Chem.*, 1879, [ii], **20**, 324) as representing the course of the reaction in his hypochlorite method of obtaining tri-iodoresorcinol:



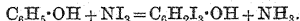
whilst in the "dry" reactions of Birnbaum (*Ber.*, 1882, **15**, 459) and Schall (*Ber.*, 1883, **16**, 1897), the authors assume that the hydrogen atom displaced by the iodine wanders in one case to the carboxyl, and in the other to the hydroxyl group, thus:



and



Finally, Willgerodt (*J. pr. Chem.*, 1888, [ii], **37**, 446) supplied for his method the equation



#### EXPERIMENTAL.

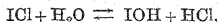
The opinion that the formation of iodophenols must be due to the presence of hypoiodous acid suggested itself to the present author during the preparation of di-iodosalicylic acid by the action of iodine monochloride on salicylic acid. It was observed, on the one hand, that the reaction did not take place in the absence of

water, whilst, on the other hand, an aqueous solution of iodine monochloride soon lost its power of combining with salicylic acid. The gradual disappearance of the "active iodine" (that is, iodine capable of attacking the phenolic molecule) from such a solution is strikingly shown in the table given below. The method employed was to add 10 c.c. of a solution of iodine monochloride in glacial acetic acid (Wijs' solution) to 100 c.c. of water; the mixture was allowed to remain at the ordinary temperature (12°) for the specified time, after which excess of sodium salicylate (5 c.c. of a 10 per cent. solution) was added to combine with the "active iodine"; this was followed after one minute by the addition of an excess of potassium iodide and titration with *N*/10-thiosulphate solution.

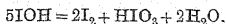
*Table showing the Rapid Decrease in the Amount of "Active Iodine" Present in Aqueous Iodine Monochloride Solution.*

Time solution was allowed to remain.	No. of c.c. of <i>N</i> /10- thiosulphate required.	"Active iodine."
0	0	27.8
10 sec.	4.1	23.7
20 "	5.8	22.0
30 "	7.3	20.5
1 min.	10.5	17.3
2 "	13.3	14.5
3 "	16.8	11.0
5 "	17.1	10.7
10 "	18.1	9.7
30 "	20.2	7.6
1 hr.	21.9	5.9
2 hrs.	23.3	4.5
16 "	25.1	2.7
24 "	26.2	1.6

How is this rapid decrease in the activity of iodine monochloride solutions explained? As is well known, iodine monochloride is partly hydrolysed in aqueous solution,



the hypiodous acid formed quickly decomposing into iodic acid and free iodine, the reaction being usually represented thus:



Now, it is highly probable that the decrease in the activity of the solution is due to this decomposition of the hypiodous acid, but, owing to our imperfect knowledge of the constitution of iodine monochloride solutions, this cannot be definitely proved. Other products of decomposition, such as the compound  $\text{ICl}_2\text{HCl}$  and

iodine trichloride, are present, and these may have a bearing on the matter.

Nevertheless, it is quite clear that the present view, which ascribes the iodination of phenols in iodine monochloride solution to the action of the iodic acid formed, is untenable, since the amount of iodophenol produced actually diminishes as the concentration of iodic acid and free iodine increases.

The next step was to investigate the formation of iodophenols in alkaline iodine solutions. In this case, thanks to the fact that the kinetics of the system iodine-potassium iodide-sodium hydroxide has been fully investigated by Schwickler (*Zeitsch. physikal. Chem.*, 1895, **16**, 303), Forster (*J. Physical Chem.*, 1903, **56**, 324), Bray (*Zeitsch. physikal. Chem.*, 1906, **54**, 563), and Skrabal (*Monatsh.*, 1907, **28**, 217; 1909, **32**, 167, 815), it is possible to show that, in such solutions, the mass of "active iodine" is at any instant equal to the amount of hypiodous acid present, thus proving them conclusively to be one and the same substance.

Without going too deeply into the kinetics of hypiodite solutions, it may be stated that the first reaction which takes place when iodine is dissolved in alkalis, namely,



attains rapidly a state of equilibrium and, in strongly alkaline solutions, the concentration of free iodine is negligible. The decomposition of the resulting hypiodous acid, on the contrary, is relatively slow, proceeding with measurable velocity. It has thus been found possible to prove that the reaction is one of the second order, the rate of change being expressed by the empirical formula

$$-\frac{d[\text{IOH}]}{dt} = \frac{[\text{I}'] + e(E)}{[\text{OH}']} \cdot ka[\text{IOH}]^2,$$

where  $E$  = total concentration of electrolytes and  $e$  = a variable factor depending on the concentration of  $\text{I}'$  and  $\text{OH}'$ .

Under special experimental conditions (when  $\text{OH}'/\text{I}' < 10$ ), the member  $e(E)$  of the equation becomes negligibly small, and the simpler formula

$$-\frac{d[\text{IOH}]}{dt} = \frac{[\text{I}']}{[\text{OH}']} \cdot [\text{IOH}]^2,$$

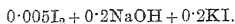
expresses the rate of change.

In the experiments which follow, the initial concentration of iodine ions and hydroxyl ions was twenty times greater than that of the hypiodous acid, so that, despite the fact that hydroxyl ions



are used up and iodine ions formed during the reaction, the ratio  $[I^-]/[OH^-]$  remained practically constant.

The method of procedure was as follows: Two hundred c.c. of a  $N/50$ -iodine solution (in potassium iodide) were rapidly mixed with an equal volume of  $0.4N$ -sodium hydroxide solution, so that the concentration of the mixture was (in mols. per litre)



Successive quantities of this solution (20 c.c. each) were removed after the specified time; excess of phenol (3 c.c. of a 5 per cent. solution) was added to combine with the "active iodine," the mixture acidified with acetic acid, and the iodine thus liberated (from the iodate and iodide) was titrated with  $N/10$ -thiosulphate.

Two explanatory remarks are here needed:

(i) The reaction between phenol and "active iodine" in the presence of excess of the former is very rapid. This may be seen by simply adding phenol to a freshly prepared solution of iodine in alkali; the yellowish-green colour of the latter immediately disappears. The speed of the reaction was also proved by allowing phenol to act for various lengths of time (from 0.5 to 20 minutes) on solutions of equal "active iodine" content; the amount of iodine used up was the same, irrespective of the time allowed before acidifying.

(ii) It is essential that acetic acid or some other weak acid is employed for acidifying the mixture. If a strong mineral acid is used, then iodine is liberated from the iodate and iodide present before the whole of the hydroxyl ions have been neutralised; hypiodous acid is consequently formed and acts on the phenol, causing an apparent increase in the amount of "active iodine." This phenomenon was first described by Kekulé, and its effect on the estimation of hypiodous acid was later eliminated by saturating the solution with carbon dioxide before acidifying (Batey, *Analyst*, 1911, **38**, 132). If acetic acid is used, the treatment with carbon dioxide becomes unnecessary; this was proved by means of blank experiments on a mixture of sodium iodate and iodide in the presence of phenol.

In the table below, the third column gives the amount of "active iodine" in terms of c.c. of  $N/100$ -iodine solution;  $k_1$ ,  $k_2$ , and  $k_3$  are constants corresponding with reactions of the first, second, and third order respectively, that is,

$$k_1 = \frac{1}{t_2 - t_1} \cdot \log \frac{c_1}{c_2}; \quad k_2 = \frac{c_1 - c_2}{(t_2 - t_1)c_1c_2}; \quad k_3 = \frac{1}{2(t_2 - t_1)} \cdot \frac{1}{c_2^2} - \frac{1}{c_1^2}$$

Table showing the Velocity of Decomposition of the "Active Iodine Compound" in Alkaline Solution.

Time.	C.c. of N/100-thiosulphate required.	c="active iodine."	$10^3k_1$	$10^3k_2$	$10^4k_3$
0	0	19.5	—	—	—
1 min.	2.0	17.5	4.20	5.8	3.15
2 "	3.7	15.8	4.43	6.14	3.65
3 "	5.0	14.5	3.73	5.67	3.8
5 "	7.4	12.1	4.43	6.84	5.35
8 "	10.1	9.4	3.66	7.90	7.5
10 "	11.3	8.2	2.96	7.78	8.9
14 "	13.0	6.5	2.52	7.96	11.0
18 "	14.1	5.4	2.01	7.83	13.4
25 "	15.2	4.3	1.41	6.80	14.1
30 "	15.8	3.7	1.30	7.53	19.0
40 "	16.5	3.0	0.91	6.31	19.1
60 "	17.3	2.2	0.67	6.01	23.8
90 "	18.7	1.5	0.53	7.07	39.7

Mean  $10^3k_2 = 6.90$

The temperature of the solution remained approximately constant ( $10.3$ — $10.7^\circ$ ) throughout the experiment.

It will be seen from the foregoing table that whilst  $k_1$  and  $k_3$  vary considerably,  $k_2$  remains satisfactorily constant over a wide range of concentration, thus proving the decomposition of the "active substance" to be a bimolecular reaction, just as is the case with hypiodous acid; the occurrence of a maximum in the value of the constant is also suggestive of the decomposition of hypiodous acid, and, finally,  $k_2$  as above determined can be shown, after applying the necessary corrections, to have the same value as the constant obtained by other authors for the rate of decomposition of hypiodous acid.

Thus, Skrabal (*Monatsh.*, 1911, **32**, 171), working at  $20.2^\circ$  with alkaline iodine-potassium iodide solutions of the same concentration as employed above, obtained for the constant of the rate of decomposition of hypiodous acid ( $k'_2$ ) the mean value  $2.63 \times 10^3$ . Two corrections are needed to make the constant found for the "active substance" comparable with that obtained by Skrabal, namely, (i) a correction for the difference in the amount of solution analysed, and (ii) a correction for the difference in the temperature.

(i) From the equation

$$k_2 = \frac{c_1 - c_2}{(t_2 - t_1)c_1c_2}$$

it is easily seen that  $k_2$  is inversely proportional to the quantity of solution analysed at a time. As this was  $89.49$  c.c. in Skrabal's

case, whilst the present author used only 19.5 c.c., the first correcting factor for the constant will be  $\frac{19.5}{89.49}$ .

(ii) The temperature-coefficient of the constant was found by Skrabal to be 2.1 (per 10°). Now,  $k_2$  was determined at 10.5° and  $k'_2$  at 20.2°, a difference of 9.7°, hence the second correcting factor for the constant is  $\frac{2.1 \times 9.7}{10}$ .

Applying these two corrections, we obtain

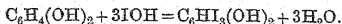
$$\begin{aligned} k_{2(\text{corrected})} &= 6.90 \times \frac{19.50}{89.49} \times 2.1 \times \frac{9.7}{10} \times 10^3 \\ &= 3.06 \times 10^3. \end{aligned}$$

The agreement between the two constants is good, bearing in mind that the "mean value" (that is, the arithmetical mean) of the constants made use of in the above calculations is only a rough approximation to their true value.

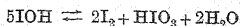
Having thus proved that the iodine which combines with the phenol in alkaline solutions is present as hypoiodous acid, and having shown that there is strong evidence for assuming that the same compound is the active substance in iodine monochloride solutions, other methods used in the preparation of iodophenols may be examined. A close scrutiny will show that in most, if not all, the processes by which these compounds are obtained, hypoiodous acid is an intermediate product.

(1) "*Iodine and Mercuric Oxide*" Method.—The formation of hypoiodous acid from these two substances in the presence of water is a matter of common knowledge (Köne, *Ann. Phys. Chem.*, 1845, [ii], 66, 300; Taylor, *Chem. News*, 1897, 76, 22).

(2) "*Hypochlorous Acid and Potassium Iodide*" Method.—The interaction between hypochlorous acid and potassium iodide, resulting in the formation of hypoiodous acid, has been studied by Klimenko (*Zeitsch. physikal. Chem.*, 1897, 23, 552, 558) and confirmed by Bray (*ibid.*, 1906, 54, 563). We may therefore substitute for Dagener's complicated formula the following:



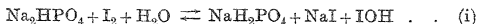
(3) "*Iodine and Iodic Acid*" Method.—The reaction



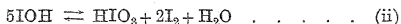
is a reversible one, and the continuous removal of hypoiodous acid by the phenol causes it to proceed towards the left.

(4) "*Iodine and Sodium Phosphate*" Method.—Iodine dissolves

in a solution of disodium hydrogen phosphate, the simplest way of formulating the reaction being



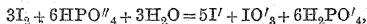
The hypiodous acid thus formed decomposes further,



so that, finally, hypiodous acid is in equilibrium on the one hand with iodine and sodium phosphate, and on the other with iodine and iodic acid. The following experiment confirms this view.

A solution of iodine and disodium hydrogen phosphate in water was prepared and allowed to remain for a fortnight, so that equilibrium was attained; the solution was still of a red colour, showing that free iodine (or, more correctly,  $\text{I}'_3$ ) was present. To one portion of this solution phenol was added, which combined with the "active iodine" and decolorised the solution; the mixture was then immediately acidified, and the iodine liberated from the iodide and iodate present was titrated with *N*/100-thiosulphate. Another portion of the same solution, after adding phenol, was allowed to remain for twenty-four hours before acidifying and titrating as above. The amount of iodine used by the phenol was in both cases the same. This is exactly what is to be expected from the equations put forward above; the addition of phenol removes the hypiodous acid present, thus disturbing both equilibria, but, since reaction (i) has a far greater velocity than reaction (ii), practically the whole of the free iodine combines with the sodium phosphate, leaving the iodate ion unaffected.

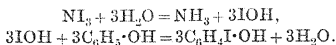
The reaction between iodine and disodium hydrogen phosphate is formulated in a rather different way by Skrabal and Gruber (*Monatsh.*, 1916, **37**, 543), who give the equation



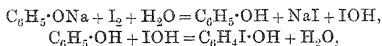
but it is obvious from the result of the above experiment that this equation does not represent the actual state of affairs; for, if it did, since the reaction is a balanced one, the removal of the free iodine by the phenol (supposing this to be possible without the intermediate formation of hypiodous acid) would cause the reaction to proceed towards the left until no more iodate ion remained in solution. This, however, is not the case, for, as we have seen, the iodate remains unaffected by the removal of the "active iodine."

(5) *Nitrogen Iodide Method*.—Selivanov (*loc. cit.*) proved that this compound yielded hypiodous acid on hydrolysis, and sug-

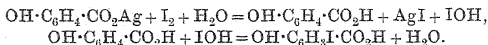
gested that the iodination is due to the last-mentioned substance. He gave the following equations:



(6) Passing on to the "dry" reactions of Birnbaum and Schall, we see that even here the formation of hypoiodous acid is not excluded. A very small quantity of moisture would be sufficient, since the water used up in the first part of the reaction is regenerated at the end. Thus in Schall's method



and in Birnbaum's



This new way of formulating the reactions obviates the necessity of assuming any intramolecular change. It should be further noted that Kekulé's criticism of Lautemann's method applies also to the last-mentioned reaction; in all probability, the formation of iodosalicylic acid does not take place on heating iodine with silver salicylate, but during the subsequent treatment. In any case, the preliminary heating is quite superfluous; if to a suspension of silver salicylate in alcohol is added a solution of iodine (in alcohol), the colour of the latter disappears quickly at first, the reaction becoming slower as the ratio between silver salicylate and iodine added approaches unity. After removing excess of iodine by shaking with mercury and filtering, there is obtained, on evaporating the alcohol, a mixture of iodosalicylic acids.

The theory that the formation of iodophenols is due to the action of hypoiodous acid is thus seen to explain the preparation of those compounds by many different methods. The real test for a useful theory, however, is its capability of predicting new phenomena and suggesting fresh lines of research. It will be seen that the above theory stands this test.

(i) For instance, it is evident that on the above theory any method of obtaining hypoiodous acid could also be used for the preparation of iodophenols; thus, it can be predicted that iodophenols will be formed by the action of silver carbonate or sulphate and iodine on phenols.

(ii) The converse proposition, that any method of preparing iodophenols may be made to yield hypoiodous acid, is probably

also true. This has been shown to be the case in the iodine and sodium phosphate method of Richard.

(iii) A further successful line of research suggested by the present theory, namely, the estimation of hypoiodous acid, will be dealt with in a later paper.

So far, the hypoiodous theory of iodination has been applied to phenolic compounds only, but many of the methods for the preparation of iodophenols, such as Kekulé's (iodine and iodic acid) and Weselsky's (iodine and mercuric oxide), have been successfully used in introducing iodine atoms into other organic compounds. Again, the formation of iodoform from alcohol and from acetone has been proved to be due to hypoiodous acid (Davenport and van't Hoff, *Rec. trav. chim.*, 1888, 1, 35; Pieroni, *Gazzetta*, 1912, 42, i, 534). It will be seen from this that hypoiodous acid as an iodinating agent has a much wider range than that outlined above. Its formation might possibly explain the action of concentrated sulphuric and nitric acids, ferric chloride, etc., as iodine carriers (Neumann, *Annalen*, 1887, 241, 84; Meyer and Schwalb, *ibid.*, 1885, 231, 195; Datta and Chatterjee, *J. Amer. Chem. Soc.*, 1917, 39, 441).

Throughout this paper, the term "hypoiodous acid" has been employed to denote the compound IOH, although, so far as its properties are concerned, "iodine hydroxide" would be a more suitable term. The latter name has been avoided, as it suggests the existence of positive iodine ions, which many chemists regard with suspicion. The work of Walden (*Zeitsch. physikal. Chem.*, 1903, 43, 385) on the conductivity of iodine in inorganic solvents, as well as other considerations (Abegg and Auerbach, "Handbuch d. anorg. Chem.," IV, (ii), 455), lend, nevertheless, considerable support to the view that iodine cations do exist. If this be really the case, then the previous statement may be modified to: the formation of iodophenols, and that of hypoiodous acid, is brought about by the presence of positive iodine ions.

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[Received, May 23rd, 1919.]

# XC.—The Influence of Hydrogen Sulphide on the Occlusion of Hydrogen by Palladium.

By EDWARD BRADFORD MAXTED.

THE activation of hydrogen by metallic catalysts is undoubtedly intimately connected with the phenomenon of occlusion; indeed, hydrogenation reactions which proceed in the presence, for instance, of palladium and free hydrogen, may also be effected by palladium containing hydrogen in the occluded state.

From this point of view the factors that determine the catalytic activity of various preparations of a given metal for hydrogenation reactions should include the occlusive power of the preparation for hydrogen, and it should follow, as a necessary sequence, that substances which exert an inhibitive effect on catalytic activity will also inhibit the occlusive power.

For the purpose of the present paper, hydrogen sulphide has been taken as a typical catalyst poison, palladium being chosen as the occluding material by reason of its high absorptive power for hydrogen.

It may be mentioned, with reference to the influence of other catalytically poisonous substances on the occluding power of palladium for hydrogen, that De Hemptinne (*Zeitsch. physikal. Chem.*, 1898, 27, 249) noticed that palladium which had been treated with carbon monoxide lost its absorptive power for hydrogen, at any rate at low temperatures. Carbon monoxide was afterwards found by Paal and Hartmann (*Ber.*, 1910, 43, 243) to inhibit the activity of this metal for the catalytic reduction of sodium picrate. The latter authors, together with Steyer (Paal and Hartmann, *Ber.*, 1918, 51, 711; Paal and Steyer, *ibid.*, 1743), showed also that mercury acts similarly on palladium hydrosols.

In the work about to be described the hydrogen-occluding power of oxygen-free palladium-black was measured before and after treatment with hydrogen sulphide, and, incidentally, data were obtained relating to the absorption of hydrogen sulphide by palladium and the stability of the absorption compound.

## EXPERIMENTAL.

The apparatus employed consisted of a small glass absorption pipette containing a known weight of palladium-black and connected by means of capillary glass tubing to a Sprengel pump and

to a gas burette respectively. This gas burette, which contained mercury, was provided with a three-way cock for the introduction of gas. The various parts of the apparatus were joined by fusion, and all stopcocks were mercury-sealed. In order to prevent access of mercury vapour to the palladium, short plugs of aluminium turnings, preceded and followed by glass-wool, were inserted in the system on each side of the absorption pipette.

The palladium was prepared in the apparatus itself by the reduction of palladium chloride at  $100^{\circ}$  by means of electrolytic hydrogen, from which the last traces of oxygen had been removed by treatment with palladinised asbestos at  $350^{\circ}$ , followed by soda-lime.

According to the measurements of Mond, Ramsay, and Shields (*Proc. Roy. Soc.*, 1897, [A], 62, 290), palladium-black occludes about 873 volumes of hydrogen at the ordinary temperature and pressure. The ease and rapidity with which this is given up varies somewhat with the nature of the palladium, but, in any case, the bulk is evolved in a vacuum at  $100^{\circ}$ . The greater part of the hydrogen occluded is taken up at once, but a slight additional absorption takes place on allowing the palladium to remain in hydrogen.

In order to avoid the possibility of changing the nature, and especially the catalytic activity, of the palladium-black by overheating, it was decided, in the present case, to regard  $100^{\circ}$  as the maximum temperature to which the palladium should be subjected, this temperature being, as already stated, sufficiently high for the extraction by exhaustion of practically the whole of the occluded hydrogen.

The first point to be studied was the constancy of the volume of hydrogen which could be removed by exhaustion at  $100^{\circ}$  or, alternatively, occluded by exposing palladium, which had been dehydrogenated in this way, to the action of fresh hydrogen at the ordinary temperature. In order to ensure uniformity in the experimental conditions, the system was in every case exhausted to a standard pressure of 3 mm. at  $100^{\circ}$ , and exhaustion was continued as long as any appreciable quantity of gas was being evolved under these conditions, the hydrogen being collected over mercury in the usual way. Subsequently, a known volume of hydrogen was admitted to the absorption tube from the gas burette and the contraction read off, the volume of the absorption pipette, including its connexions, having been determined previously.

Table I summarises the results of eight experiments carried out in this way. The measurements numbered 5 and 6, also those numbered 7 and 8, were made with fresh quantities of palladium-black, which in every case weighed 0.6 gram, corresponding with



1 gram of palladium chloride. The volume of gas evolved or occluded is in every case reduced to normal temperature and pressure.

TABLE I.

No. of expt.	Vol. of hydrogen evolved on exhaustion.	Vol. of hydrogen subsequently occluded.
	C.c.	C.c.
1	41.3	40.0
2	40.2	40.5
3	41.9	41.1
4	41.4	—
5	41.5	40.6
6	41.9	—
7	41.6	40.5
8	41.5	—

The average volume of hydrogen evolved or occluded under the above conditions is thus about 41 c.c., corresponding with 68.5 c.c. per gram of palladium.

Dry hydrogen sulphide, prepared by the action of heat on a solution of magnesium hydrosulphide, was now allowed to pass into the exhausted reaction tube in place of hydrogen and to remain in contact with the palladium, from which the occluded hydrogen had previously been removed by exhaustion at 100°. Occlusion of a certain amount of the gas took place at once, and was followed by a slower and continuous absorption of a secondary nature. It had previously been ascertained that hydrogen sulphide, provided it is dry and free from oxygen, does not attack either mercury or aluminium at a rate sufficient to influence the measurements.

Table II summarises an absorption experiment with 0.6 gram of palladium.

TABLE II.

Time.	Vol. H <sub>2</sub> S absorbed.
	C.c. at N.T.P.
1 min. ....	0.2
5 min. ....	7.1
10 „ ....	7.5
3 hr. 20 min. ....	10.4
18 hr. ....	12.2
40 „ ....	13.5

By interrupting the absorption after a suitable time of contact, palladium containing various proportions of hydrogen sulphide could be obtained. The hydrogen sulphide thus absorbed was not removed to any great extent by exhaustion at the ordinary temperature, this being especially the case when the hydrogen sulphide content of the palladium was comparatively low, and, on passing hydrogen into the

exhausted absorption pipette, occlusion of this gas no longer took place.

Under the conditions employed, it was not found possible, in view of the velocity of the primary occlusion of hydrogen sulphide by palladium, to prepare specimens of the metal containing less than about 13.5 c.c. of hydrogen sulphide per gram, corresponding with an absorption of about 8 c.c. for the 0.6 gram of palladium taken for each experiment, and the minimum volume of hydrogen sulphide required for the total inhibition of the hydrogen-occluding properties of palladium could therefore not be determined. This figure is, however, certainly less than 14 c.c. per gram of palladium.

On exhausting the palladium containing hydrogen sulphide at 100° a volume of gas, approximately equal to that of the hydrogen sulphide contained in the preparation, was evolved, but was found on analysis to consist almost entirely of hydrogen, the sulphur of the absorbed gas being retained by the palladium.

Table III records three results of this nature.

TABLE III.

No. of expt.	Wt. of Pd in grams.	Vol. of H <sub>2</sub> S absorbed.	Occlusive power for hydrogen.	Vol. of gas evolved in a vacuum at 15°.	Vol. of gas subse- quently evolved in a vacuum at 100°.	Analysis of total gas evolved	
						H <sub>2</sub> . C.c.	H <sub>2</sub> S. C.c.
1	0.6	8.2	Nil.	0.1	8.2	8.3	—
2	0.6	13.5	"	1.1	12.8	13.7	0.2
3	0.6	17.7	"	2.3	16.4	17.4	1.3

An interesting observation was made with respect to the specific influence of the nature of the sulphur absorption compound on the occlusive power of the palladium for hydrogen, in that, whilst about 8 c.c. of hydrogen sulphide are sufficient to inhibit completely the occlusive power for hydrogen of 0.6 gram of palladium, the equivalent quantity of sulphur, which remains behind after exhaustion at 100°, is by no means sufficient to prevent completely the occlusion of hydrogen.

In order to study quantitatively the influence of sulphur in the latter form, measurements were made of the volume of hydrogen which was capable of being absorbed or evolved by various specimens of palladium of known sulphur content, the hydrogen portion of the absorbed hydrogen sulphide having been previously extracted by exhaustion at 100°.

The results obtained are tabulated below, the measurements of occlusive power having been carried out under similar conditions to

the experiments recorded in table I. The sulphur content was determined both by measuring the volume of hydrogen sulphide which had been absorbed, subtracting any small quantity evolved as such during the preliminary exhaustion at  $100^{\circ}$ , and also, as a check, after measuring its occlusive power, by dissolving the preparation in aqua regia and precipitating as barium sulphate. In order to obtain a preparation containing as high a proportion of sulphur as 0.0328 gram to 0.54 gram of palladium, corresponding with an absorption of 23.0 c.c. of hydrogen sulphide, an absorption period of about three weeks was necessary.

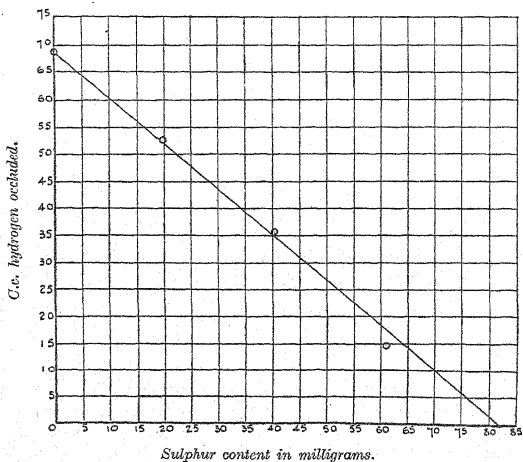


TABLE IV.

No. of expt.	Wt. of Pd. Gram.	Wt. of sulphur content. Gram.	Occlusive power for hydrogen.	
			Vol. absorbed. C.c. at N.T.P.	Vol. subsequently evolved. C.c. at N.T.P.
1	0.6	0.0117	31.7	31.6
2	0.6	0.0117	31.8	32.4
3	0.6	0.0117	31.3	31.0
4	0.6	0.0117	30.7	—
5	0.6	0.0242	21.2	21.6
6	0.54	0.0328	8.4	8.2
7	0.54	0.0328	8.0	7.9
8	0.54	0.0328	7.7	7.9

On plotting the above results graphically, it will be seen that the mean occlusive power for hydrogen is approximately a linear function of the sulphur content, and that each atom of sulphur renders almost exactly four palladium atoms incapable of occluding hydrogen, the remainder of the palladium being capable of occluding normally. The accompanying curve, which shows this relation, refers to 1 gram of palladium.

Whilst any discussion respecting the constitution of the compound formed by the decomposition of hydrogen sulphide by palladium does not fall within the scope of the present paper, it may be noted that the occlusive power of a preparation of this kind may be predicted by assuming a compound  $\text{Pd}_4\text{S}$  to be formed, and ascribing to the residual palladium its normal power of absorption. There is, however, insufficient evidence to justify the assumption of the actual formation of this or any compound, and it may be mentioned in this connexion that palladium foil was found to remain untarnished by pure dry hydrogen sulphide both at the ordinary temperature and at  $100^\circ$ .

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## XCL.—*The Critical Solution Temperature of a Ternary Mixture as a Criterion of Purity of Toluene.*

By KENNEDY JOSEPH PREVITÉ ORTON and DAVID CHARLES JONES.

THE use of binary critical solution temperatures in the determination of purity has become well known since Crismer (*Bull. Soc. chim. Belg.*, 1895, **9**, 145; 1896, **10**, 312; 1904, **18**, 1; 1906, **20**, 294) originally demonstrated the great delicacy of the critical solution temperature of the alcohol-petroleum binary in detecting the presence of, and in estimating the amount of, water in the alcohol. As a means of distinguishing rapidly between various fats and oils and of testing the purity of liquid substances, the use of critical points has been considerably developed. The occurrence, however, of the critical points of binary mixtures in convenient ranges of temperature is relatively rare, and hence the applicability of the method is for practical purposes comparatively limited.

This disadvantage largely disappears in a ternary mixture. If

a ternary mixture is used, a far wider field of stable organic liquids is available as constituents; by adjusting the composition of the mixture of liquids chosen, the critical points can be brought into a convenient range of temperature.

The objection which has been mainly urged against a ternary mixture for this purpose (Timmermans, *Zeitsch. physikal. Chem.*, 1907, **58**, 129) is the great accuracy with which the constituents must be measured in making up the mixture, and, as a result, the definite use of a ternary mixture has received no application in the laboratory as a criterion of liquid purity. On the other hand, a considerable number of miscibility points of systems virtually ternary, or of a higher order, have been suggested as rough qualitative methods in industrial work (compare Salamon and Seaber, *J. Soc. Chem. Ind.*, 1915, **34**, 461; Shrewsbury, *Analyst*, 1909, **34**, 348; 1914, **39**, 529; Armani and Rodano, *J. Soc. Chem. Ind.*, 1912, **31**, 912 (abstract); Tortelli and Fortini, *Gazzetta*, 1911, **41**, i, 173; Fryer and Weston, *Analyst*, 1918, **43**, 3; Parkes, *ibid.*, 82). In a strictly binary mixture, commonly no fine adjustment of the proportions of the two constituents is necessary in order to find the temperature of the critical solution point.

Industrial toluene, which has passed through a full process of purification by treatment with sulphuric acid and so forth, and careful rectification, may yet contain a certain proportion of admixture, which may be taken to consist in the main of paraffin hydrocarbons of like boiling point (compare recent papers on allied subjects by various authors, *J. Soc. Chem. Ind.*). The toluene distils completely within  $0.5^{\circ}$ , but its density is about 0.23 per cent. lower than that of pure toluene.

In this investigation, we have had as an object the establishing by means of a change in the critical solution temperature ("c.s.t.") of a ternary mixture a general criterion of the purity of toluene, and specifically to detect and to estimate petroleum in toluene.

Toluene will give a ternary c.s.t. with many solutions, as, for example, certain aqueous alcohol, aqueous acetone, aqueous acetic acid, etc., the temperatures of critical solution of which lie in convenient ranges when the proportion of water is rightly chosen. The best solution for this purpose will have the following characteristics: It must be stable under ordinary conditions, and its composition accurately and conveniently determined; the two components of the solution must be easily obtained pure; and the critical-point phenomena must be distinct.

Aqueous acetic acid and toluene form a ternary mixture which meets the conditions just laid down, the c.s.t. of which can by proper choice of the proportion of water be brought into the region

of 0—50°. Unlike formic acid, which with benzene gives a binary c.s.t. at 73·2° (Ewins, T., 1914, 105, 350), anhydrous acetic acid, propionic acid, and *n*-butyric acid are completely miscible with benzene and toluene at the ordinary temperature.

Waddell (*J. Physical Chem.*, 1898, 2, 232) examined the ternary mixture benzene-acetic acid-water at 25° and 35°, which, as would be expected, very closely resembles the system toluene-acetic acid-water. Both are very similar to the system chloroform-acetic acid-water (Wright, *Proc. Roy. Soc.*, 1891, 49, 174; 1892, 50, 375).

In a ternary as in a binary mixture, the sensitiveness of the critical points to impurity in one constituent of the mixture is determined by the relative solubility of the impurity and the one constituent in the other constituents of the mixture. Thus, the remarkable delicacy of Crismer's method is to be attributed to the great difference of solubility of the water and alcohol in petroleum. Hence the effect of an impurity in the toluene is various, depending on the relative solubilities of the impurity and toluene in the acetic acid solution. Thus we find that the presence of benzene leads to a relatively small fall in the temperature, of xylene to a relatively small rise. The fall in temperature is approximately a linear function of the concentration of benzene, and the rise of that of xylene. With a given aqueous acetic acid (water=10·1 per cent., m. p. 2·77°), when the proportions of the two constituents are 0·6232 c.c. of aqueous acetic acid and 0·4958 c.c. of the other (see later), the critical solution temperatures are:

TABLE I.

	c.s.t.
Benzene .....	-3·3°
Toluene .....	23·6°
<i>m</i> -Xylene .....	52·9°
Bromobenzene .....	34·5°
<i>p</i> -Bromotoluene.....	65·4°

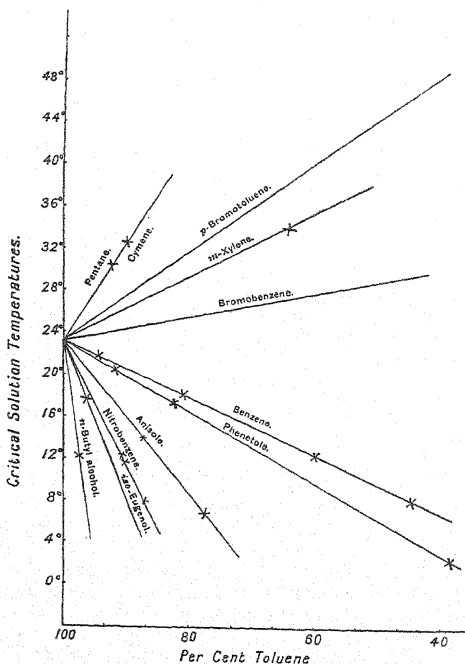
It will be noted that the melting point of benzene is a surer guide to the presence of toluene than the c.s.t. One per cent. of toluene depresses the melting point by 0·6°, but only raises the c.s.t. by 0·27°. The c.s.t. is comparable with the melting point in detecting the presence of xylene in benzene. In the absence of melting points, the critical solution temperatures are good guides to the presence of xylene in toluene, and vice versa.

Other substances with a greater solubility in water than benzene have a still greater depressing effect on the c.s.t.; to the presence in toluene of such relatively soluble substances as *iso*amyl and *n*-butyl alcohols, the c.s.t. becomes extremely sensitive, and is greatly depressed by small quantities. The curves shown in Fig. 1

will sufficiently illustrate the effect of various substances which we have examined.

The solubility of paraffin hydrocarbons in acetic acid and in water is very much less than that of toluene. The presence of petroleum raises, therefore, the c.s.t. of the systems toluene-acetic

FIG. 1.



acid-water and benzene-acetic acid-water in a very marked way. If the toluene contains 1 per cent. of petroleum (b. p. 124–132°, octane), the c.s.t. (23.5°) is raised by 1.6°. Since the temperature of critical solution can be read with certainty to 0.1° at the range of temperature used, such small proportions as one-sixteenth per

cent. of paraffin can be detected in benzene, toluene, xylene, and the like, and the proportion estimated to the same degree of accuracy. For paraffin in benzene, the method is far more delicate than the melting point. The fact that the same aqueous acetic acid can be used in the three hydrocarbons named is an additional advantage.

In the homologous series of paraffin hydrocarbons, the solubilities are very similar, but the progressive decrease of solubility as the series is ascended in the effect on the c.s.t. of the toluene-acetic acid-water system is obvious (table II).

TABLE II.

Substance present as impurity in toluene.	Elevation or depression of c.s.t. for 1 per cent. of substance.
Benzene .....	-0.27°
Xylene .....	0.29°
Cymene .....	0.90°
Pentane .....	0.90°
Hydrocarbon fractions mainly b. p. 109-110° ...	1.4°
(Octane) 124-132° ...	1.6°

If it be assumed that the complete substitution of octane for toluene is accompanied by a proportional rise in the c.s.t., the c.s.t. of pure octane with this particular aqueous acetic acid will be about 160°. Since increase in the concentration of the acetic acid solution used lowers the temperature of critical solution, it appears probable that some paraffin hydrocarbons would give binary critical solution temperatures with more concentrated—glacial—acetic acid. We have determined (approximately) the values of certain fractions.

TABLE III.

Hexane. Acetic acid, m. p. 15.6° .....	c.s.t.
Hexane. " " 15.0° .....	1°
Hydrocarbons boiling at 205-225°	25°
" " 225-240°	59°
" " 240-264°	66.5°
Acetic acid, m. p. 16.15°	81.0°

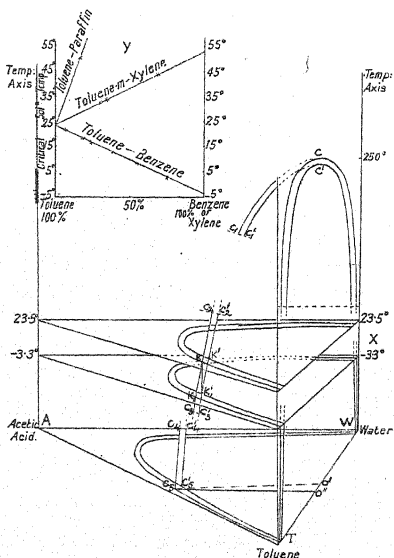
This similarity in solubility relation among the homologous fatty paraffins, which is the cause of this small difference in the values of the c.s.t., may be contrasted with the widely varying relations among the fatty acids.

In Fig. 2 (in which we have followed Roozeboom, "Heterogene Gleichgewicht," Vol. III.),  $CC_1C_2C_4C_5$  represents the critical curve of the system toluene-acetic acid-water from the binary c.s.t. of



toluene-water,  $C$  (which we find to lie approximately at  $250^\circ$ , under pressure), through the ternary c.s.t.'s on the isothermal binodal curves; the base of the prism corresponds with an isothermal just below  $0^\circ$ . Similarly,  $C'C'_1C'_2C'_3C'_4C'_5$  represents the corresponding critical curve for benzene. In the enlarged inset ( $X$ ),  $K$  and  $K'$  represent the ternary c.s.t.'s of the toluene and benzene systems, respectively, at the isothermal  $23.5^\circ$ , whilst  $K_1$  and  $K'_1$  represent the c.s.t.'s at  $-3.3^\circ$ .

FIG. 2.



The percentage composition of the system at  $K$  is: toluene, 39.34; acetic acid, 54.52; water, 6.14.

The percentage composition of the system at  $K'_1$  is: benzene, 39.72; acetic acid, 54.22; water, 6.06.

Waddell's values for the benzene system at  $25^\circ$  are: benzene, 39.6; acetic acid, 54.22; water, 7.6.

If in a system the composition of which is represented by  $K$  the

toluene is gradually displaced by the same volume of benzene, the critical phenomenon exhibited by the system remains always distinct up to the complete replacement of toluene, that is,  $KK'_1$ , a line parallel to the temperature axis, cannot be detected as having left the region of the critical curve. The great similarity in the solubility relations of benzene and toluene would account for this behaviour. Moreover, the temperature of the (now) quaternary c.s.t. is linearly related to the increasing proportion of benzene in the system (inset *Y*, Fig. 2). Quite analogous results were found to hold in the case of xylene, the critical curve being as much without that of toluene as that of benzene within, and also, as the diagram (*Y*) shows, replacement of toluene by xylene causes a linear corresponding alteration in the c.s.t.

On the other hand, the critical curves of aqueous acetic acid-petroleum and aqueous acetic acid-toluene, owing to the greater difference in solubility, lie very much further apart. It is probable that in cases of this kind, substitution of petroleum for toluene would lead the system away from the curve, but up to 17 per cent. of petroleum the critical phenomena remain very distinct, and the relation between the proportion of petroleum and the elevation of the c.s.t. is linear (Fig. 6).

*Relation between Melting Point of the Acetic Acid and the  
c.s.t. with Toluene.*

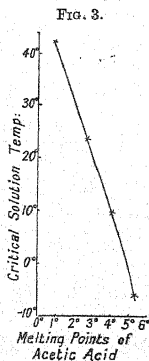
The c.s.t. of the ternary system toluene-acetic acid-water rises proportionally to the increase in the quantity of water over a small range—3.5 per cent. and the elevation of the c.s.t. is almost linearly related to the depression of melting point of the acetic acid (Table IV, and Fig. 3.)

TABLE IV.

M.p. of aqueous acetic acid.	Percentage of water.	c.s.t.
5.45°	8.2	-5.9°
4.2°	9.0	9.8°
2.77°	10.1	23.5°
0.9°	11.7	41.9°

(The percentage of water is obtained from Faucon's numbers, *Ann. Chim. Phys.*, 1910, [viii], 19, 84).

Similarly, the c.s.t. of the binary system alcohol-petroleum (Crismer) and benzene-formic acid (Ewins) rises proportionally to the concentration of water added.



In Fig. 2, let  $C_5$  represent the critical point on the lowest binodal curve,  $ATW$ ; on replacing acetic acid by water, keeping the proportion of toluene constant, the composition of the system follows the line  $CO''$  parallel to the acetic acid-water line,  $AW$ .  $CO'$ , the projection of the critical curve on the isothermal plane, represents the whole series of critical compositions up to the binary c.s.t. of toluene and water. Hence, unless  $O'$  approximates to  $O''$  in position (assuming  $CO'$  to be a straight line), addition of water soon takes the system away from the region of the critical curve. The phenomenon of critical solution, then, will not appear when the temperature of miscibility is observed. It must be emphasised that in our experiments the distance travelled by the system as water replaces acetic acid, along  $CO''$ , is relatively very small. The system is still found sufficiently near to the critical curve for an obvious exhibition of the critical phenomena.

*Measurement of the Constituents.*—In using the change in the c.s.t. of a ternary mixture produced by an impurity for the purpose of estimating the impurity, such as we are suggesting, accuracy of measurement of the quantity of the constituents is of the greatest importance (compare Timmermans, *loc. cit.*). Thus, as an illustration, the numbers given in the table of the temperature of the critical solution of the system toluene-acetic acid-water show the effect of an increase in the proportion of toluene (pure) of less than 1 per cent.

TABLE V.

Aqueous acetic acid.	Toluene.	Difference.	c.s.t.	Difference.
0.6232	0.5006	0.0144	24.05°	
0.6232	0.4862	0.0144	22.4°	1.65°

The difference 1.65° would correspond with the presence of 1 per cent. of petroleum.

In the figure (2), the point  $K'_1$  represents the composition of the ternary c.s.t. of benzene-acetic acid-water. Any change in the proportion of any one constituent causes the composition of the system to move either into a region of heterogeneity within the binodal curve or of unsaturation and homogeneity without the curve. In systems such as benzene-acetic acid-water (or toluene-acetic acid-water), the solubility relations of which change slowly with alteration of temperature, a considerable temperature change would be required before the miscibility point of the new system is reached. In other words, the sensitiveness of the c.s.t. to slight variations in composition is a consequence of the great extension of the figure along the temperature axis.

The very great importance of accuracy of proportions of the

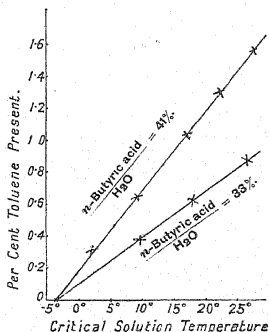
constituents in a binary as well as in a ternary mixture is well illustrated by a perhaps extreme case which we have observed. Fig. 4 shows the effect of addition of toluene to two mixtures of *n*-butyric acid and water, one containing 41 and the other 33 per cent. of the acid. These two mixtures both give the same miscibility temperature ( $-3.7^{\circ}$ ) in the critical region, owing to the long, flat top of the solubility curve (Faucon, Rothmund, *Zeitsch. physikal. Chem.*, 1908, **63**, 57, and Timmermans). The solubility curve of the system alcohol-petroleum has a similar form.

If one regards the toluene as an impurity in the binary system butyric acid-water, each curve (Fig. 4) may be taken to show the effect of increasing concentration of the impurity on the binary c.s.t. If, however, it is desired to estimate by the elevation of the c.s.t. the proportion of impurity, it will be seen that it is obviously essential that the proportions in which the constituents are taken shall be exactly known. If the proportion of *n*-butyric acid is 41 per cent., then the presence of 1 per cent. of toluene causes a rise in the c.s.t. of  $21^{\circ}$  (Fig. 4), whereas if the proportion of *n*-butyric acid is 33 per cent., 1 per cent. of toluene gives a rise of  $35^{\circ}$ .

Alternatively, let the concentration of toluene be fixed at 1 per cent., then a variation of the proportion of butyric acid from 41 to 33 per cent. will lead to a change in the c.s.t. of  $15^{\circ}$ . Yet in the absence of toluene both acid-water mixtures will have the same miscibility temperature.

This example brings out very clearly the necessity of using exact proportions of the constituents when the binary c.s.t. is being used as a criterion of the degree of purity. Only when the liquid is finally purified are the exact proportions of less importance, since before that stage is reached the system is not binary, but of a higher order. Thus, in the use which is commonly made of the alcohol-petroleum binary to estimate the proportion of water in the alcohol, it is essential, even for small quantities of water, that certain definite proportions of petroleum and aqueous alcohol should be used.

FIG. 4.



It is obviously of first importance, if the method is to become of practical utility, that the proper degree of accuracy should be combined with rapidity and simplicity of manipulation. We find that a remarkably high degree of accuracy can be reached by using small, carefully constructed pipettes, one for the solution of fixed concentration and the other for the liquid the purity of which is to be tested. The manipulation and the method of estimating petroleum in toluene which we recommend have been tested in the analytical laboratory of a large chemical works, and have received a very favourable report as giving accurate and consistent results in the hands of the average manipulator.

#### EXPERIMENTAL.

*Apparatus.*—The accurate measurement of (1) the solution used, (2) the liquid the purity of which is to be tested, is the first consideration in using this method. Weighing of liquids is a lengthy and difficult operation. We find that for small volumes the degree of accuracy which can be reached with properly constructed pipettes is quite remarkable. The diagram (Fig. 5) shows the form and the dimensions of the pipettes we have used. The essentials in the form and use of the pipettes are as follows: (1) The tip of the pipette is drawn into a fine capillary tube, so that the liquid may be held with certainty to the mark, whilst the time for delivery is about one minute for volumes 0.5—1 c.c. (2) The stem of the pipette should be of small diameter, since with wide tubes, (a) change in pressure of the finger causes a very appreciable variation in the height of the meniscus, an effect which is very marked with a pipette having an ordinary tip; (b) error in adjustment of the meniscus is magnified. (3) After drawing in a liquid and adjusting to the mark, the outside of the tip should be gently wiped with a silk duster, at the end of which operation the liquid fills the pipette from the mark to the end of the tip. (4) When the pipette has ceased delivering, the capillary tip (in contact with the glass) is emptied by a gentle blow. (5) Every care is taken to have a clean glass surface; finally, the pipette is washed out with distilled water and dried by a current of dust-free air.

The following illustrations will emphasise the extremely small error entailed in the use of these pipettes. A "5 c.c." pipette, terminating in a fine capillary tube, delivered its content of water in two minutes. At a definite temperature, it delivered in five successive trials 4.95979 c.c., 4.95986 c.c., 4.95995 c.c., 4.95966 c.c., 4.96011 c.c.; the volumes are calculated from the weights of water delivered. It will be seen that the maximum variation between

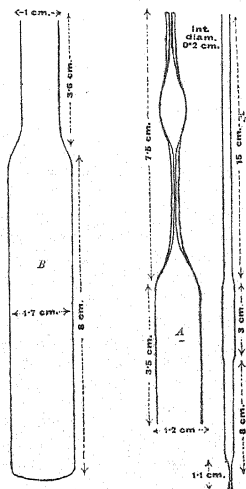
any two readings is 0.00045 c.c., and the maximum variation from the arithmetic mean 0.00024 c.c., or 0.005 per cent.

A "2 c.c." pipette, which delivered its content of water in only ten seconds, lengthened, however, in delivery to one minute, gave the following weights of water in five successive experiments: 2.0146, 2.0146, 2.0172, 2.0138, 2.0172 grams. Here the maximum variation reaches 0.0034 gram, and from the arithmetic mean is 0.0017 gram, or 0.08 per cent.

A very small pipette, of the same type, but smaller than those we have generally used, delivering its content of water very slowly—in about one minute—gave the following readings in four successive experiments: 0.2524 c.c., 0.2524 c.c., 0.2525 c.c., 0.2527 c.c. The maximum variation between any two readings is 0.0003 c.c., and from the arithmetic mean 0.0002 c.c., or 0.1 per cent.

We have used small pipettes of various content, but for the apparatus in which we have observed the c.s.t. of the toluene-aqueous acetic acid and similar systems, pipettes of from 0.4 to 0.7 c.c. capacity are required. The aqueous acetic acid pipette delivered 0.6232 c.c., and the toluene pipette 0.4958 c.c. These are the quantities of our aqueous acetic acid (see later) and pure toluene, which we found to exhibit the phenomena of critical

FIG. 5.



solution in the clearest and most obvious way. The maximum variation from the mean is 0.0002 c.c., and hence in one pipette the maximum error may amount to 0.03 per cent., and in the other to 0.04 per cent. An error of measurement of 0.001 c.c., that is, five times the actual maximum variation observed, produces a difference of  $0.1^\circ$  in the c.s.t. of toluene, and would correspond with an error of 0.0125 per cent. in the estimation of paraffin.

The experimental tube has the form and dimensions shown in the diagram (Fig. 5). The cap (A) is fastened on the tube (B) by a short piece of rubber tubing. This tube is attached to the

thermometer by rubber rings, and the whole combination is used as a stirrer of the bath.

The thermometer is a standard instrument, preferably graduated in twentieths, but a graduation in tenths will suffice for most purposes.

The bath is a glass beaker of 2 litres capacity filled with water and heated by a small gas burner of the Argand type. The flame is simply and effectively regulated by a screw clip compressing a rubber tubing; the adjustment is very delicate when the rubber and slip are made fast to the bench, and hence the temperature is raised with the deliberation necessary as the temperature of critical solution is attained.

*Determination of c.s.t.*—At the ordinary temperature, the contents of the experimental tube are in two layers, the lower layer being mainly composed of aqueous acetic acid. As the temperature rises, the mutual solubility of the two layers increases, and they intermingle more readily as their densities, viscosities, etc., approach the same value, the suspensions of one layer in the other taking place in smaller drops requiring longer to separate. Gradually, striations appear through the body of the liquid, which is now distinctly opalescent. The temperature of the bath should now be rising at the approximate rate of  $1^{\circ}$  in five minutes. The striations become more and more delicate as the layers approach identity in every respect, and faint beginnings of blue fluorescence appear. This fluorescence deepens in tone, and when evident throughout the liquid, the striations being still clearly visible, the temperature of the bath must be raised more slowly at the approximate rate of  $0.1^{\circ}$  per minute. Close observation will now show the disappearance of the striations and greatly increased fluorescence. This temperature is taken as the critical solution point. The clearness with which one can see the thermometer scale through the liquid is a good test (first mentioned by Rothmund, *loc. cit.*) for observation in these final stages. The reading can now be repeated by cooling the bath very slightly, say  $0.2^{\circ}$ , and again taking the critical solution temperature. Readings may be repeated as often as desirable with the same mixture.

*Materials.*—The pure acetic acid was fractionated through an eight-bulb still-head. A considerable quantity was placed in a special double-stoppered bottle, and water added to bring it to the composition desired. We have used two solutions containing approximately 10.1 and 11.7 per cent. of water, and melting approximately at  $2.77^{\circ}$  and  $0.9^{\circ}$  respectively. To obtain a correct reading of the melting points of such dilute acetic acids is a very difficult matter (compare Faucon, *loc. cit.*). The temperature

cannot be determined within  $0.02$ — $0.03^{\circ}$ . The acid melting at " $2.77^{\circ}$ " gave a c.s.t. with pure toluene at  $23.5^{\circ}$ , and that melting at " $0.9^{\circ}$ " a c.s.t. at  $41.9^{\circ}$ . A difference in melting point of  $0.01^{\circ}$  of the acetic acid leads to a difference of the c.s.t. with pure toluene of  $0.1^{\circ}$ .

Since pure toluene can be readily obtained in quantity, it is better to prepare an aqueous acetic acid approximately of the desired composition, and then to determine the c.s.t. with pure toluene, rather than deduce the c.s.t. of the system from the melting point of the aqueous acetic acid.

*Pure Toluene.*—A quantity of toluene which had been prepared in the usual way from recrystallised toluene-*p*-sulphonic acid was shaken with saturated sodium carbonate solution, washed with distilled water twice, and dried over granulated calcium chloride (which does not, however, reduce the saturation point below  $0^{\circ}$  unless the liquid is simultaneously cooled). It was then fractionated through an eight-bulb still-head, and the large middle fraction refractionated. The "standard" toluene thus obtained has the characteristic that, on distillation, the first 10 c.c., the main fraction, and the last 10 c.c. yield the same c.s.t. with a given aqueous acetic acid. No change in the c.s.t. of the standard toluene could be observed after treatment with phosphoric oxide and refractionation.

The toluene has  $D_{12.6}^{12.6} 0.87417$ ; Perkin (T., 1896, **69**, 1241) gives  $D_{12.6}^{12.6} 0.87403$ .

*Benzene.*—The benzene was obtained by fractionating a specimen (m. p.  $5.4^{\circ}$ ) until the fractions (first, main, and final) gave a constant c.s.t. with the standard "acetic" acid melting at " $0.9^{\circ}$ ," when quantities identical with those taken for toluene were used. The value of the c.s.t. is  $14.3^{\circ}$ . With acetic acid melting at " $2.77^{\circ}$ " the c.s.t. is  $-3.3^{\circ}$ .

### *The Presence of Paraffin Hydrocarbons in Toluene.*

For the purpose of studying the effect of the presence of paraffin hydrocarbons in toluene, the paraffin was obtained from American petroleum.

After shaking with sulphuric acid (95 per cent.) (which removes the olefines, Colman and Yeoman, *J. Soc. Chem. Ind.*, 1919, **38**, 57; Thole, *ibid.*, 39) until a fresh quantity of sulphuric acid remained uncoloured, the hydrocarbon was warmed and shaken with a mixture of nitric and sulphuric acids for many hours.

After washing with aqueous alkali and then with water, and drying with granular calcium chloride, it was distilled through an



eight-bulb still-head. After several fractionations, the two fractions, b. p. 109—110° and b. p. 124—132°, were used for admixture with toluene.

In determining the c.s.t. of the mixture, the pipette delivering 0.6232 c.c. was used for the aqueous acetic acid, and the pipette delivering 0.4958 c.c. for the mixture of toluene and petroleum. The results are summarised in the following table (VI) and graphically shown in Fig. 6.

TABLE VI.

A. Paraffin boiling at 124—132°. Aqueous acetic acid melting at "0.9°" and containing about 11.7 per cent. of water (Fig. 6).

Paraffin. Per cent.	c.s.t.	Paraffin. Per cent.	c.s.t.
0.0	41.8°	8.98	56.05°
1.054	43.65°	10.17	57.6°
1.31	43.9°	14.45	64.2°
2.08	45.4°	17.17	68.5°
3.926	48.1°		
6.17	51.4°		

B. Paraffin boiling at 109—110°. Aqueous acetic acid melting at "0.9°" and containing about 11.7 per cent. of water (Fig. 6).

Paraffin. Per cent.	c.s.t.
2.317	45.1°
4.09	47.5°
9.28	54.85°
14.54	62°

C. Paraffin boiling at 124—132°. Aqueous acetic acid melting at "2.77°" and containing 10.1 per cent. of water.

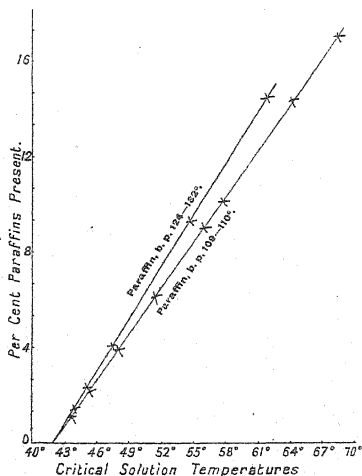
Paraffin. Per cent.	c.s.t.	Paraffin. Per cent.	c.s.t.
0	23.5°	6.17	33.05°
1.054	25.2°	8.98	37.6°
1.31	25.5°	10.17	39.0°
2.08	26.8°	17.17	50.1°
3.926	29.7°		

It is to be remarked that the presence of 1 per cent. of the paraffin boiling at 124—132° produces the same rise, 1.6°, in the c.s.t. whether aqueous acetic acid melting at "0.9°" or at "2.77°" is used.

*Estimation of Petroleum in Industrial Toluene.*

Several specimens of industrial toluene were examined, including some which had been purified to meet the Government standard, and boiled within  $0.5^{\circ}$ . Before determining the c.s.t., the toluene was shaken with small quantities of sulphuric acid (95 per cent.) until the acid no longer became coloured. It was then shaken with aqueous sodium hydroxide, washed with water, dried with calcium chloride, and fractionated through an eight-bulb still-head.

FIG. 6.



(The "Government" toluene gave a c.s.t. of  $44.5^{\circ}$  with "0.9" acetic acid; a specimen of toluene of French official origin, a c.s.t. of  $44.3^{\circ}$ ; and a specimen of toluene supplied by English distilleries, a c.s.t. of  $44.0^{\circ}$ .)

Three fractions were collected of the material which distilled within  $0.5^{\circ}$ , a small first fraction, a main fraction, and a small residue. The c.s.t.'s with aqueous acetic acid (m. p. " $0.9^{\circ}$ ") were respectively  $44.35^{\circ}$ ,  $44.4^{\circ}$ , and, with the residue,  $45.2^{\circ}$ , whereas pure toluene gives a value of  $41.8^{\circ}$ .

Thus but little elimination of impurity is effected by the fractionation; the c.s.t. of the 15 c.c. residue is only  $0.8^{\circ}$  above the main fraction, which has a value  $2.6^{\circ}$  above that of pure toluene. The chemical treatment and the fractionation would remove all impurity save paraffin hydrocarbons of similar boiling points, which, as is well known, are commonly found in the usual sources of toluene. The presence of xylene as the cause of the high value of the c.s.t., beyond a trace, is, apart from all else, completely excluded, inasmuch as an elevation of  $2.6^{\circ}$  would require from 8 to 9 per cent. of xylene (Fig. 2, Y).

If paraffin of about the boiling point  $124-132^{\circ}$  is taken as the main impurity, then, from the data given in the foregoing, the toluene contains 1.6 per cent. (by weight) of paraffins. If paraffin of about the boiling point  $109-110^{\circ}$  is the impurity, the toluene contains 1.85 per cent.

Some additional light is thrown on the problem by comparison of the densities, as the following results show. The specimen of industrial toluene, having a c.s.t. of  $44.4^{\circ}$ , has  $D_{15.4}^{15.4}$  0.8721. Pure toluene containing 1.6 per cent. of paraffin boiling at  $124-132^{\circ}$  has the same c.s.t. and  $D_{15.4}^{15.4}$  0.8718, whilst toluene containing 1.85 per cent. of paraffin boiling at  $109-110^{\circ}$  has again the same c.s.t. but  $D_{15.4}^{15.4}$  0.8710.

It may be inferred that the toluene contains somewhat less than 1.6 per cent. of paraffins, which distil over a range probably somewhat above  $124-132^{\circ}$ .

Direct estimation of the paraffin by Spielmann and Jones's (*J. Soc. Chem. Ind.*, 1917, **36**, 490) modification of Wilson and Roberts's method does not apparently give a very accurate result with such a small proportion of paraffin.

The paraffin was isolated in a similar way from a large volume of toluene distilling within  $0.5^{\circ}$ ; it had  $D_{15.4}^{15.4}$  0.7312. The density of octane (b. p.  $125.5^{\circ}/760$  mm.) is given as 0.7188 at  $0^{\circ}$ , and of nonane (b. p.  $149.5^{\circ}/760$  mm.) as 0.733 at  $0^{\circ}$ .

We think it may be fairly claimed that the critical solution temperatures of aqueous acetic acid with industrial benzene, toluene, or xylene which have been fully purified afford an accurate means of determining the content of paraffin hydrocarbons.

We intend to pursue the study of ternary mixtures, and especially of the use of the critical solution temperatures of such mixtures as a criterion of purity of liquids.

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[Received, July 22nd, 1919.]

## XCII.—*Thiocyanoacetone and its Derivatives and Isomerides.*

By JOSEPH TCHERNIAC.

THIOCYANOACETONE,  $\text{SCN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$ , was first obtained by the action of monochloroacetone on barium thiocyanate in alcoholic solution (Hellon and Tcherniac, *Ber.*, 1883, **16**, 349). Later it was found that the reaction takes place in the absence of alcohol when the crystallised barium salt is intimately mixed with monochloroacetone (Tcherniac, *Ber.*, 1892, **25**, 2623). Further investigation has shown that an aqueous solution of any thiocyanate of the alkalis (except that of ammonia) or of the alkaline earths can be used with advantage. As an example, the preparation by means of the sodium salt may be described.

To 92.5 grams (1 mol.) of monochloroacetone,\* 191.4 c.c. (1.1 mols.) of a 46.55 per cent. solution of sodium thiocyanate were added, and the mixture was stirred for ten hours. The temperature rose about  $25^\circ$ , and a brown oil gradually separated. The whole product, oil and aqueous solution, was completely extracted with ether. The ethereal extract, which contained an appreciable quantity of dissolved thiocyanate, was shaken with successive quantities (10 c.c.) of water until the wash-water gave only a slight reaction with ferric chloride. The united washings, which contained some thiocyanoacetone, were reserved for addition to the final preparation before the ether extraction.

The ether was distilled off from a water-bath at the lowest temperature possible. Fifty c.c. of distilled water were added to the residue, and the whole was heated in a water-bath to  $40$ — $50^\circ$  under 14 mm. pressure. The water distilled over, carrying with it some chloroacetone and its impurities, together with a very small quantity of thiocyanoacetone (0.35 gram).

The residue was dried in a vacuum over sulphuric acid, and analysis showed it to be nearly pure thiocyanoacetone (108—109 grams = 95 per cent. yield).

*Purification of Thiocyanoacetone.*—Thiocyanoacetone cannot be distilled without decomposition in the ordinary vacuum of the water-pump—about 14 mm. (Tcherniac, *Ber.*, 1892, **25**, 2625). It distils, however, unaltered under a pressure of about 1 mm. A portion of the thiocyanoacetone prepared as above was placed in an Anschütz distillation flask with collar and sealed-on receiver.

\* Prepared by Fritsch's method (*Ber.*, 1893, **26**, 597), using magnesia instead of marble, and carefully fractionated. It contained traces only of dichloroacetone.

Ground in the neck of the receiver were a U-tube filled with calcium chloride and potassium hydroxide, and a Hittorf tube. The apparatus was exhausted by means of a mercury pump, the flask being heated in a water-bath. With purple light in the Hittorf tube, most of the oil, evaporating from the surface without visible boiling, passed over at  $73.5-74.5^\circ$ , and was collected separately. The distillate was a highly refracting, colourless oil having  $D_{20}^{25} 1.1892$ . Analysis gave results showing close agreement with the formula  $C_4H_5ONS$ .

On keeping, especially in the light, the oil gradually became yellow, and finally dark-coloured.

*Action of Hydrochloric Acid on Thiocyanacetone.*

It has already been shown that dilute aqueous hydrochloric acid does not produce any great alteration in thiocyanacetone (Tcherniac, *Ber.*, 1892, **25**, 2618).

When 5 per cent. of its weight of hydrogen chloride is led into thiocyanacetone, kept cool, a crystalline magma is formed which liquefies on keeping. On extraction with ether, the thiocyanacetone is recovered apparently unaltered. A quite different result is obtained when the substance is saturated with hydrogen chloride.

Thiocyanacetone (115 grams:1 mol.) was saturated with hydrogen chloride (70 grams), the whole being cooled with running water. After the resulting magma had completely liquefied, the syrup was dissolved in 500 c.c. of water, and the solution extracted with ether. The latter left on distillation 70 grams of a pale brown oil, which was distilled under 14 mm. pressure from a water-bath, and gave 40 grams of a colourless distillate passing over at  $69^\circ$ .

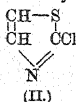
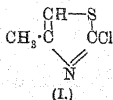
In another preparation the solution was distilled in a current of steam instead of being extracted with ether, and gave half the weight of the thiocyanacetone taken.

The oil was washed with dilute sodium hydroxide solution, dried over calcium chloride, and distilled. By far the greater part passed over at  $167-167.5^\circ/754.4$  mm.

Found: C=35.99; H=3.2; N=10.22; Cl=26.43. S=24.38.

$C_4H_4NClS$  requires C=35.95; H=2.99; N=10.48; Cl=26.59; S=23.97 per cent.

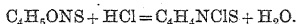
Apparently this substance is 2-chloro-4-methylthiazole (I), a



homologue of 2-chlorothiazole (II) (Schatzmann, *Annalen*, 1891, **261**, 10), the boiling point of which is 144—144.5°.

2-Chloro-4-methylthiazole is a colourless oil boiling at 167—167.5°/754.4 mm. and 69°/14 mm.; it has  $D_{15}^{25}$  1.2992. It possesses a characteristic odour resembling that of pyridine, and slightly alkaline properties; thus, it dissolves in concentrated hydrochloric acid, but not in the dilute acid. It is comparatively stable; after boiling for twelve hours with a methyl-alcoholic solution of sodium methoxide, only one-twentieth of its chlorine was removed, and the bulk of the oil remained unaltered. In this respect it differs from chlorothiazole, which is said to retain the chlorine very loosely. This is not an isolated fact. The chemical behaviour of the members of the thiazole group is often so radically different from that of their methylated homologues (see Schatzmann, *loc. cit.*) that serious doubts must arise as to their analogy of structure.

It was found that of the 70 grams of hydrogen chloride absorbed by the thiocynoacetone, 14 grams had been consumed in the reaction



The residue from the distillation of the ethereal extract, together with the aqueous solution from which the oil had been extracted, after neutralisation with sodium carbonate and further extraction with ether, yielded 25 grams of "hydroxymethylthiazole" (after purification by crystallisation).

The action of alcoholic hydrogen chloride on thiocynoacetone will be described later.

#### *Thiocynoacetone and Ammonia.*

The so-called hydroxymethylthiazole, which was obtained accidentally by Hantzsch and Weber (*Ber.*, 1887, **20**, 3127) in an attempt to prepare thiocynoacetone, owed its formation to the circumstance that they had used sodium carbonate for salting out the thiocynoacetone. As has been shown (*Ber.*, 1892, **25**, 2619), all alkaline substances possess the power of converting thiocynoacetone into its isomeride. Aqueous ammonia produces exactly the same result. Hantzsch's statement (*Annalen*, 1888, **249**, 7) that the chief product of the action of ammonia on thiocynoacetone is aminomethylthiazole (thiocyanopropimine) is devoid of all foundation, as may be seen from the following experiments.

Thiocynoacetone (115 grams:1 mol.) was dissolved in 1500 grams of water, the solution cooled, and 50 c.c. of 20 per cent.

ammonia were added. Heat was evolved, and a yellow resin separated. After forty hours, the solution was filtered, and to the filtrate 172 c.c. of 25 per cent. hydrochloric acid were added, much carbon dioxide being evolved.

The acid solution was extracted with ether in the author's automatic apparatus (this vol., p. 1090), and the ethereal extract evaporated in the water-bath. The brown, syrupy residue was heated in a vacuum on the water-bath, when some water possessing the pungent odour of thiocyanic acid distilled over. The distillate gave the thiocyanate reaction and gradually deposited a small quantity of radially grouped yellow needles, which became dark at about 150° and decomposed at about 200° (perthiocyanogen?).

The residue from the distillation (63.5 grams) was boiled for some time with ether under a reflux condenser. After repeated crystallisations, about 25 grams of pure "hydroxymethylthiazole" were obtained from the solution, together with a small quantity of the yellow substance above-mentioned.

If any aminomethylthiazole had been formed, it must have remained in the hydrochloric acid solution which had been extracted with ether. This solution was therefore rendered alkaline with sodium hydroxide and completely extracted in the apparatus. The ethereal extract left on distillation 1.732 grams of a dark syrup only partly soluble in hydrochloric acid. The hydrochloric acid solution was filtered, warmed with animal charcoal to 50°, and again filtered. After several days, a black mud was deposited, which was filtered off. The filtrate was warmed with charcoal (0.5 gram) and again filtered. To the filtrate, hydrochloric acid was added, together with platinic chloride in excess, and the whole left to remain overnight, when the yellow precipitate was collected. When dry, it weighed 1.040 grams, proved insoluble in water or alcohol, and melted at about 220°. (Found: Pt=30.36.  $(C_4H_6N_2S, HCl)_2PtCl_4$  requires Pt=30.34 per cent.)

Assuming this to be pure double salt, it corresponds with 0.477 gram of aminomethylthiazole from 115 grams of thiocyanacetone. Moreover, as thiocyanate is formed in the reaction, there is no reason to think that even this minute quantity of the base owes its origin to anything more than the well-known action of ammonium thiocyanate on thiocyanacetone (Norton and Tcherniac, *Ber.*, 1883, 16, 345).

In view of the foregoing results, Hantzsch's explanation (*loc. cit.*, p. 26; compare Beilstein, "Handbuch der organischen Chemie," IV, 518) of the formation of aminomethylthiazole (thiocyanopropimine), namely, that by the action of ammonium thiocyanate on chloroacetone, thiocyanacetone is first formed, and is

then converted by combination with free (!) ammonia into aminomethylthiazole, must be regarded as invalid.

*The Isomerides of Thiocynoacetone: Hydroxymethylthiazole, or  $\alpha$ -Methylrhodim.*

For reasons to be stated later, the so-called hydroxymethylthiazole will henceforth be known as  $\alpha$ -methylrhodim.

The author has shown (*Ber.*, 1892, **25**, 3648) how  $\alpha$ -methylrhodim is best prepared from thiocynoacetone. The same method may be used for its preparation direct from chloroacetone.

To 92.5 grams of monochloroacetone, 1500 grams of water, 125 grams of potassium thiocyanate (or the equivalent amount of the sodium salt), and 30 grams of sodium hydrogen carbonate are added. The mixture is shaken from time to time and allowed to remain for ten days. A brown resin is gradually deposited, and the aqueous solution is filtered off and warmed to 45°. Twenty grams of animal charcoal are then added, and the mixture is left to remain for two hours and shaken from time to time. It is then filtered, and the filtrate extracted with ether in the apparatus. On an average, there accumulated in the flask containing the ether 33 grams of white needles, which, after being washed with ether, melted at 102—103°. From the ethereal solution, a further 14 grams were obtained, making in all 47 grams, that is, approximately 41 per cent. of the theoretical yield.

Instead of extracting with ether, a tedious operation in the absence of an automatically working apparatus, the aqueous solution can be evaporated in a vacuum from a water-bath, care being taken to keep the temperature of the bath below 60° until there remain about five parts of water for one of  $\alpha$ -methylrhodim. On cooling, 75—80 per cent. of the substance will crystallise out, and the mother liquor may be further concentrated.

When less water or sodium hydrogen carbonate is used in the preparation, the yield is smaller.

Impure  $\alpha$ -methylrhodim is best purified by recrystallisation from five times its weight of water at 55—60°. Thus, 41 grams of the crude product were dissolved in 205 grams of water, the solution being shaken with charcoal and filtered warm. The first crop yielded 32 grams of needles melting at 102—103°.

By utilising the mode of formation from ammonium thiocarbamate (observed by Marchesini, *Gazzetta*, 1893, **23**, ii, 442), the preparation of  $\alpha$ -methylrhodim can be much more satisfactorily accomplished than by the above method. The way there followed, namely, heating in an alcoholic solution, is unsuitable as a method

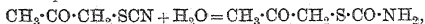


of preparation. It required thorough modification to obtain from it a simple and practical method.

Ammonium thiocarbamate,  $\text{NH}_2\cdot\text{CO}\cdot\text{S}\cdot\text{NH}_2$ , is easily obtained pure by leading carbonyl sulphide into alcoholic ammonia cooled with ice. The gas is readily absorbed, and a white, crystalline powder is soon deposited, which is rapidly collected, washed with alcohol, and dried in a vacuum over sulphuric acid. Two hundred and fifty c.c. of 4.14 per cent. alcoholic ammonia yielded 18.82 grams of the dry salt.

The thiocarbamate (14.3 grams: about 0.15 mol.) was dissolved in a little water, ice added, and 12 c.c. of monochloroacetone (13.95 grams = 0.15 mol.) were mixed with the solution, and the flask was imbedded in ice. Soon a violent reaction took place, when the chloroacetone dissolved, the ice melting within the flask. The slightly yellow liquid was filtered, and the filtrate (74 grams) left to remain overnight. It set to a paste of yellowish needles (12.85 grams, dry) melting at  $101\text{--}102^\circ$ . From the filtrate 3.2 grams were obtained, the total of more than 16 grams representing a yield of 93 per cent. The product was easily purified by one crystallisation from water.

This result, compared with the complications attending the preparation from thiocynoacetone, renders highly improbable the intermediate phase



suggested by Hantzsch and Weber (*Ber.*, 1887, 20, 3128) as part of the mechanism of the isomerisation.

*$\alpha$ -Methylrhodim and Methyl Sulphate: Dimethylrhodim.*

$\alpha$ -Methylrhodim (115 grams: 1 mol.) was dissolved in 500 c.c. of 2*N*-sodium hydroxide, and 95 c.c. of methyl sulphate (1 mol.) were gradually added, cooling with water. The solution was extracted with ether in the apparatus. The ether left 122.6 grams of a yellow oil, which solidified on cooling. When dissolved in its own volume of water, it showed a lower critical solution temperature. The slightest warmth, even that of the hand, induced separation into two layers, which mixed again on cooling. The solution was shaken with 10 grams of charcoal, filtered, the turbid filtrate concentrated in a vacuum at  $35^\circ$ , when it became clear again, and the concentration continued until the solution in the distillation flask weighed 145 grams. (A small quantity of oil distilled over with the water.) To the cold solution a tiny crystal from a previous preparation was added, and the whole left over sulphuric acid in a vacuum. Large crystals were gradually formed and removed

from time to time. In all, 65 grams were collected and recrystallised from a small quantity of water.

In another preparation, the crude product remaining after the distillation of the ether was drained on the vacuum pump from the oil which it contained, and was then washed with ether.

A quantity of crude product (20 grams) which had been kept for two years and had become brown and viscid was purified in the following manner. It was dissolved in water with the addition of 20 c.c. of *N*-sodium hydroxide and extracted with ether. The extract was almost colourless, and the aqueous solution yellowish-brown. The ether was evaporated, and left 17.322 grams of oil which soon solidified, the temperature rising to 46°. The substance was dissolved in its own weight of water at 25°, and when the solution assumed the ordinary temperature (17°), a fragment of a crystal was added. Overnight, large crystals separated (10.359 grams, m. p. 48–49°), and from the mother liquor a further crop was obtained (5.4 grams).

The original yellowish-brown solution which had been extracted with ether was acidified with hydrochloric acid and again extracted. The ether left 1.442 grams of a yellowish-brown oil which did not crystallise.

It appears from the foregoing that it will simplify the purification to add sodium hydroxide to the aqueous solution containing the product of the interaction of the sodium salt of  $\alpha$ -methylrhodim and methyl sulphate before extracting with ether.

The substance after repeated crystallisations reached a maximum melting point, and was then analysed.

Found: C=46.22; H=5.81; N=10.52; S=25.20.

$C_5H_7ONS$  requires C=46.51; H=5.43; N=10.85; S=24.80 per cent.

The substance is therefore dimethylrhodim,

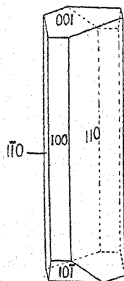


It is very readily soluble in water or ether, and crystallises from the former in large, transparent prisms or plates melting at 49–50°.

The strong tendency of this substance to form large, well-defined crystals created a desire for the determination of its crystallographic characteristics.

This work has been kindly undertaken for me by Mr. G. M. Bennett, to whom I tender my warmest thanks. His report is as follows:

"Crystallographic examination of dimethylrhodim. Crystal system: monoclinic; holohedral class. Habit:



R R\*

prismatic, with elongation parallel to the *c*-axis. Axial angle =  $98^{\circ}11'$ . Axial ratios :  $a:b:c = 2.580:1:1.874$ . Forms observed : (100), (110), (001), (10 $\bar{1}$ ). There is a well-marked cleavage in the plane (100).

"The following are the regular measurements:

	Observed.	Calculated.
100-110	$68^{\circ}37'$	—
110- $\bar{1}10$	$42^{\circ}51'$	$42^{\circ}46'$
100-001	$81^{\circ}49'$	—
001-101	$38^{\circ}40'$	$38^{\circ}43'$
100-10 $\bar{1}$	$59^{\circ}28'$	—
001-110	$86^{\circ}58'$	$87^{\circ}1'$
101-110	$79^{\circ}11'$	$79^{\circ}20'$

"The faces of the crystals were rather dull through abrasion, particularly the small ones, so that some of the values are a little uncertain."

#### *Hydrolysis of Dimethylrhodim.*

The substance (2.58 grams) was heated with 10 c.c. of hydrochloric acid (D 1.19) for two hours at  $140^{\circ}$  in a sealed tube. There was considerable pressure on opening the tube, and the escaping gas had an odour of hydrogen sulphide and mercaptan. The contents of the tube were washed out with water and distilled, when some oil, apparently chloromethylthiazole, passed over with the water. The residual liquid was rendered alkaline and distilled into hydrochloric acid so long as the evolved vapours gave an alkaline reaction.

Part of the hydrochloride was obtained as such. After crystallisation, it gave  $\text{Cl} = 52.26$ , whilst  $\text{CH}_3 \cdot \text{NH}_2 \cdot \text{HCl}$  requires  $\text{Cl} = 52.29$  per cent. The remainder was converted into the platinumchloride, which contained  $\text{Pt} = 41.12$ , whilst  $(\text{CH}_3 \cdot \text{NH}_2 \cdot \text{HCl})_2 \cdot \text{PtCl}_4$  requires  $\text{Pt} = 41.32$  per cent.

No other base than methylamine was observed, and the total amount represented more than 90 per cent. of the theoretical.

It appears, therefore, that the methyl group introduced into the molecule of  $\alpha$ -methylrhodim is attached to the nitrogen atom.

An attempt to prepare an *O*-ether from  $\alpha$ -methylrhodim by the action of methyl iodide on the silver salt was unsuccessful. The alkaline solution is, indeed, precipitated by silver nitrate, but the precipitate consists chiefly of silver sulphide, part of the substance being destroyed.

#### *$\alpha$ -Methylrhodim and Phosphorus Pentachloride.*

$\alpha$ -Methylrhodim, which can be crystallised from warm phosphoryl chloride without any alteration, was dissolved in that solvent, a little more than the equivalent quantity (1 mol.) of phosphorus

pentachloride added, and the mixture heated to  $50^{\circ}$ . Hydrogen chloride was evolved, and a product was formed which was purified by repeated crystallisation from benzene.

Found:  $S=21.74$ .

$C_4H_4ONClS$  requires  $S=21.40$  per cent.

The chloride consists of pale brown, radially grouped acicular crystals melting and decomposing at  $144^{\circ}$ . It dissolves in dilute sodium hydroxide solution with a slight evolution of heat and the loss of the whole of its chlorine. On saturating the alkaline solution with carbon dioxide, a fine mud is deposited, which shrinks on drying to brown, brittle nodules (about 70 per cent. of the weight of the chloride) not melting at  $220^{\circ}$ .

The constitution of this product will be considered later.

*Thiocyanoacetone and Alcoholic Hydrogen Chloride:*  
 *$\beta$ -Methylrhodim.*

Hydrogen chloride (75 grams) was led into a mixture of thiocyanacetone (115 grams:1 mol.), alcohol (115 grams), and water (18 grams). On the following day, the mixture was placed in a vacuum over sulphuric acid and sodium hydroxide, and allowed to remain for several days. The brown residue (162 grams), containing a few crystals, was removed with water and extracted in the automatic apparatus. After some time, crystals began to appear both in the flask of boiling ether and in that of the aqueous solution. The extraction was continued for eight days until the crystals in the latter had disappeared. By that time, an abundance of crystals had accumulated in the ether flask, along with some brown oil. The latter was decanted with the ether, and the crystals were washed with ether and alcohol. The crystals (38 grams, dry) were dissolved under a reflux condenser in 760 grams of boiling water, charcoal was added, and the solution filtered hot. On cooling, white crystals were gradually deposited (33 grams).\*

The same substance was formed when  $\alpha$ -methylrhodim was left to remain for a long time in contact with concentrated hydrochloric acid, preferably in the presence of alcohol. A mixture of 11.5 grams of  $\alpha$ -methylrhodim, 50 grams of hydrochloric acid (D 1.19), and 25 c.c. of alcohol yielded more than 3 grams of the substance.

Found:  $C=41.41$ ;  $H=4.54$ ;  $N=11.93$ ;  $S=28.11$ .

$C_4H_5ONS$  requires  $C=41.74$ ;  $H=4.35$ ;  $N=12.17$ ;  $S=27.83$  per cent.

\* From the mother liquors chloromethylthiazole (18 grams) and  $\alpha$ -methylrhodim (25 grams after purification) were obtained.

The substance, another isomeride of thiocyanacetone, is named  $\beta$ -methylrhodim.

$\beta$ -Methylrhodim is deposited from hot water as a white, crystalline powder; from alcohol by slow crystallisation in stout, colourless, quadratic plates melting at  $183-184^{\circ}$ . It dissolves in about 20 parts of boiling water and in about 475 parts at  $15^{\circ}$ . It is fairly readily soluble in boiling alcohol, less so in cold, and sparingly so in ether. When submitted to prolonged extraction in the apparatus with a relatively small quantity of ether, it accumulates in the boiling solvent and separates gradually in fine, colourless, transparent plates.

It is readily soluble in alkalis, and is precipitated therefrom by acetic acid.

*$\beta$ -Methylrhodim and Hydrochloric Acid.*

$\beta$ -Methylrhodim (3.45 grams) was heated with 30 c.c. of hydrochloric acid (D 1.19) for two hours at  $100^{\circ}$  in a sealed tube. There was no pressure on opening the tube, and the yellow solution yielded 3 grams of  $\alpha$ -methylrhodim, together with a minute quantity (0.045 gram) of white crystals, which separated from the ethereal extract. They shrank, became brown at  $250^{\circ}$ , and did not melt at  $265^{\circ}$ . Whilst, therefore,  $\beta$ -methylrhodim is formed from  $\alpha$ -rhodim under the influence of cold hydrochloric acid, the inverse conversion takes place almost completely at a higher temperature.

*Thiocyanacetone and Sodium Hydrogen Sulphite:  
isoMethylrhodim.*

After prolonged heating of thiocyanacetone on the water-bath, it was found to contain a crystalline substance, different from the then known derivatives. The same substance was obtained by the action of alkali hydrogen sulphites on thiocyanacetone, and, after many attempts, a method was perfected which allowed it to be prepared with certainty and in a state of purity.

The action of free sulphur dioxide may be described first.

A solution of thiocyanacetone (11.5 grams) in 150 grams of water absorbed 37 grams of sulphur dioxide, of which 26 grams were lost when the solution was left in a vacuum at the ordinary temperature. The solution was then extracted with ether, and yielded only 0.45 gram of a yellow oil. The extracted solution was concentrated to 20 c.c. in a vacuum on a water-bath at  $40^{\circ}$ . The residue, which still had the odour of sulphur dioxide, was again treated with ether, and yielded 8.24 grams of fairly pure thiocyanacetone.

It would appear, therefore, that a sulphonic acid possessing a certain degree of stability is formed.

Quite different is the behaviour of thiocyanacetone towards alkali hydrogen sulphites when they contain no free sulphur dioxide.

Thiocyanacetone (230 grams:2 mols.) was added to a mixture of 2150 c.c. of water and 360 c.c. of a 27·8 per cent. solution of sodium hydrogen sulphite, which was neutral towards methyl-orange. The temperature rose 11°. The solution was shaken with charcoal and filtered rapidly through a folded filter. After two days there was an abundant crystallisation. The crystals were collected (72 grams, dry) and recrystallised (66·5 grams, dry) from 1450 grams of boiling alcohol.

Found: C=41·70; H=4·29; N=12·05; S=27·66.

$C_4H_5ONS$  requires C=41·74; H=4·35; N=12·17; S=27·83 per cent.

The substance has therefore the composition of thiocyanacetone, and is a third isomeride of that compound; it will be named *isomethylrhodim*.

*isoMethylrhodim* is remarkable for its great power of crystallisation and sparing solubility in cold water or alcohol. It requires 16 parts of boiling and 400 parts of cold alcohol. It crystallises from alcohol in white, long, brilliant, interwoven needles melting at 127—128°.

It dissolves slowly in dilute sodium hydroxide solution, but with decomposition. When the orange-coloured solution is treated with carbon dioxide, it evolves hydrogen sulphide and deposits after a time a sparingly soluble salt (sodium cyanurate?).

The sodium hydrogen sulphite used for the preparation of *isomethylrhodim* does not act solely as a catalyst. Part of the aqueous mother liquor from which the *isomethylrhodim* had been separated, and containing a trace only of sulphuric acid, was distilled with hydrochloric acid, and the distillate collected in a receiver containing water and sodium hydrogen carbonate. A portion of the distillate was oxidised with bromine, and the sulphuric acid produced was estimated gravimetrically. The result revealed the consumption of 56·13 grams of sodium hydrogen sulphite, a little more than one molecule for four molecules of thiocyanacetone.

#### *Preparation of isoMethylrhodim from Chloroacetone.*

Monochloroacetone (92·5 grams:1 mol.) was stirred for two and a-half hours with 190 c.c. of a 47 per cent. solution of sodium

thiocyanate, cooling with water, when sodium chloride began to be deposited. A solution of 60 grams of crystallised potassium hydrogen sulphite in 300 c.c. of water was added, when nearly all dissolved, and the stirring was continued for half an hour. After two days, the yellow needles (44.27 grams, dry, m. p. 124—125°), containing some oil, were separated and recrystallised twice from 700 and 500 grams, respectively, of boiling alcohol, yielding, finally, 34.285 grams of white needles melting at 127—128°.

When sodium hydrogen sulphite solution was used instead of the crystallised potassium salt, the yield was much lower.

The various quantities of oil obtained in the different preparations were found to consist chiefly of thiocycanoacetone.

*isoMethylrhodim and Hydrochloric Acid: Dithiazylamine.*

Concentrated hydrochloric acid acts slowly on *isomethylrhodim* at the ordinary temperature, but rapidly on heating. *isoMethylrhodim* (23 grams) was boiled with 200 c.c. of concentrated hydrochloric acid and 66 c.c. of water under reflux for twenty minutes, when some hydrogen chloride was evolved. About half the liquid was then distilled off, a yellow oil passing over with the distillate. From the latter, ether extracted 1.5 grams of oil.

To the orange residue in the distillation flask, 300 grams of water were added, the whole was boiled for some time, filtered from a yellow resin, the solution treated with charcoal, and filtered hot. On cooling, faint yellow, efflorescent needles were deposited (10.2 grams, anhydrous), which were dissolved in 115 c.c. of boiling 8 per cent. hydrochloric acid, the solution being shaken with charcoal and filtered hot. On cooling, long, yellow, prismatic needles separated, which were collected and washed with the same dilute acid. After being pressed between filter paper, they weighed 13.1 grams; they contained water of crystallisation, as well as some hygroscopic moisture. In a vacuum over sulphuric acid and sodium hydroxide, they effloresced to a powder and lost about 27 per cent. of their original weight. For analysis, some of the substance was recrystallised as above.

Found: C=39.09; H=4.53; N=16.69; Cl=14.57; S=26.09.

$C_8H_9N_3S_2.HCl$  requires C=38.79; H=4.04; N=16.97; Cl=14.34; S=25.86 per cent.

Found:  $H_2O=27.00$ .

$C_8H_9N_3S_2.HCl.5H_2O$  requires  $H_2O=26.67$  per cent.

The substance is a hydrochloride, the acid of which can be estimated by titration.

The compound crystallises in pale yellow needles which easily

lose their water of crystallisation, crumbling to a fine, yellow powder which does not melt at  $250^{\circ}$ , but appears to sublime and decompose.

One part of the anhydrous salt is soluble in 46.25 parts of water at  $26^{\circ}$  and in 3—4 parts of hot water. The hydrate is fairly soluble in concentrated and sparingly so in dilute hydrochloric acid. The latter is a very convenient solvent for its purification; thus, one part of the hydrate (equal to 0.733 part of the anhydrous salt) dissolves in about 9 parts of hot 10 per cent. hydrochloric acid, whilst it requires more than 130 parts of the cold acid of the same strength. It separates from alcohol as a yellow, crystalline powder.

*The Base,  $C_8H_9N_3S_2$ .*

The aqueous solution of the hydrochloride is precipitated by alkali hydroxides, when these are not in excess, or by alkali carbonates.

The hydrochloride (57 grams) was dissolved in 2600 grams of water, the slightly turbid solution filtered, 115 c.c. of 2*N*-sodium hydroxide were added to the filtrate, and the white, voluminous, caseous precipitate was collected (48 grams, dry, instead of the theoretical 48.6 grams, m. p.  $148-150^{\circ}$ ).

The 48 grams were recrystallised from 340 grams of hot alcohol. On cooling, yellowish, asbestos-like needles were deposited (38.4 grams, dry, m. p.  $150-151^{\circ}$ ). The mother liquor yielded a further quantity (8.8 grams).

For analysis, the substance was twice recrystallised from a mixture of benzene and light petroleum.

Found: C=45.37; H=4.57; N=19.69, 19.74.

$C_8H_9N_3S_2$  requires C=45.49; H=4.27; N=19.90 per cent.

The base crystallises from the above solvent in almost white, spherical clusters of needles; from alcohol, in felt-like aggregates of long, silky needles melting at  $153-154^{\circ}$ . It dissolves in about 5 parts of hot and 37 parts of cold alcohol. It is insoluble in water or alkali carbonates, but soluble in alkali hydroxides.

*Determination of Molecular Weight by the Cryoscopic Method.*

Weight of solute. Gram.	Weight of solvent. Grams.	Nature of solvent.	$\Delta$ .	M.W.
0.1077	12.945	Benzene	0.13°	313.6
0.1659	"	"	0.20	313.8
0.1107	19.630	Nitrobenzene	0.105	351.6
0.1674	"	"	0.172	357.5

Average      334.0

$C_8H_9N_3S_2$  requires M.W. = 211.



*Determination of Molecular Weight by the Ebullioscopic Method.*

0.1939 Gram of substance in alcohol. Constant for 100 c.c. = 15.6.

Rise in temperature.	Grams in 100 c.c.	M.W.
0.110°	2.938	416.7 (?)
0.137	2.620	298.3
0.120	2.365	307.4
0.107	2.154	314.0
	Average	334.0

The average happens to be the same by both methods, but the individual results are too divergent to make the average appear conclusive; it corresponds approximately with 1.5 times the simple formula  $C_8H_9N_3S_2$ . Since this formula cannot be multiplied by 1.5, the only recourse is to double it, unless, indeed, we admit molecular aggregation in solution, a phenomenon which does not appear uncommon in the case of complicated compounds.

A determination by Zerewitinov's method (*Ber.*, 1907, **40**, 2023; 1908, **41**, 2233) of the active hydrogen in the base, in pyridine solution, cold or hot, gave respectively 1.274 and 1.476 atoms of hydrogen per molecule of the formula  $C_8H_9N_3S_2$ . Of course, it is not impossible that the substance undergoes a far-reaching change under the influence of magnesium methyl iodide.

As will be seen later, when the structure of the group  $C_4H_4NS$  is discussed, the base is probably dithiazylamine,  $(C_4H_4NS)_2NH$ .

*Examination of the Oil.*

The oil, the second product of the action of hydrochloric acid on isomethylrhodim, was distilled under 14 mm. pressure several times, when it passed over at 94—97° (mostly at 96—97°), each time leaving a residue and undergoing slight decomposition. It would no doubt distil unchanged under still lower pressure.

As was to be expected, the results of the analysis were only approximate.

Found: C=49.14; H=5.67; S=45.24.

$C_8H_4S$  requires C=50.00; H=5.55; S=44.44 per cent.

*Determination of Molecular Weight by the Cryoscopic Method.**In Glacial Acetic Acid.*

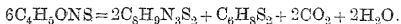
Weight of solute. Gram.	Weight of solvent. Grams.	Δ.	M.W.
0.1530	20.91	0.205°	139.2
0.3792	"	0.515	136.3
0.5322		0.720°	137.8

$C_8H_4S_2$  requires M.W.=144.

The formula,  $C_3H_4S$ , has therefore to be doubled. A determination by the ebullioscopic method gave the number 188.

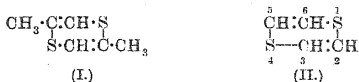
The compound is a colourless, highly refractive oil having a characteristic odour reminiscent of turpentine. It dissolves in concentrated sulphuric acid, yielding an orange-coloured solution which is not precipitated by water.

The formation of this substance, jointly with that of the base, may be accounted for as follows:



About two-thirds of the quantity of the base to be expected from this equation is obtained and one-third of the amount indicated for the compound,  $C_6H_8S_2$ .

The structural formula of  $C_6H_8S_2$  may be represented by I, and



if the ring (II) be termed thiën, the compound,  $C_6H_8S_2$ , will be 2:5-dimethylthiën.

#### *isoMethylrhodim and Methyl Iodide.*

Five sealed tubes each containing 7 grams of *isomethylrhodim*, 10 grams of methyl iodide, and 20 grams of methyl alcohol were heated for three hours at  $125^\circ$ . On opening the tubes, the escaping gas had a fishy odour and contained carbon dioxide. The brown liquid, containing needle-shaped crystals, was removed with methyl alcohol and distilled from a water-bath. The residue (53.75 grams) was boiled with 750 c.c. of water, the solution filtered from a black tar, and boiled with charcoal. On cooling, a mixture (3.835 grams) of compact crystals (4) and of fine needles was deposited and separated mechanically; the latter proved to be unaltered *isomethylrhodim*.

The mother liquor was reduced by distillation to about 250 c.c. Along with the water, a small quantity of a malodorous oil and some solid matter passed over, which gave an ethereal extract of 0.622 gram.

The aqueous residue from the distillation was boiled with animal charcoal and filtered hot. On cooling, crystals (1.4 grams) similar to (4) were deposited.

The filtrate was now concentrated to 50 c.c., and yielded a further quantity (2.67 grams) of the same substance. The final mother liquor (B) will be mentioned later.

The three crystallisations of (A), together weighing about 7 grams, were dissolved in 400 grams of boiling water, the solution treated with charcoal, and filtered hot. The crystalline deposit (4.405 grams, dry) was recrystallised from 135 grams of water, and yielded 3.467 grams of long, colourless, massive crystals not melting at 265°. When heated on platinum, they sublimed without melting (Found: C=27.80; H=2.53; N=33.09. CHON requires C=27.90; H=2.33; N=32.72 per cent.).

The substance has therefore the composition of cyanuric acid, the properties of which it possesses. Thus, it gives Hofmann's reaction with sodium hydroxide and Wöhler's with copper sulphate.

The final mother liquor (B) was distilled in a vacuum to dryness, and the residue (23.51 grams) crystallised from alcohol. White plates (13.07 grams) were obtained which volatilised completely at about 220° with the evolution of iodine (Found: C=18.15; H=4.54; S=15.47; I=61.54, 62.13. C<sub>3</sub>H<sub>3</sub>Si requires C=17.65; H=4.41; S=15.68; I=62.25 per cent.).

The compound is therefore trimethylsulphine iodide.

It thus appears that under the influence of methyl iodide at a comparatively low temperature, *isomethylrhodim* undergoes complete disruption.

### *Comparative Examination of the Three Rhodims.*

#### *Determination of Molecular Weight by the Cryoscopic Method.*

##### *α-Methylrhodim*, m. p. 103—104°.

Weight of solute. Gram.	Weight of solvent. Grams.	Nature of solvent.	Δ.	M.W.	Average.
0.1342	21.385	Nitrobenzene	0.26°	173.8	—
0.0845	"	"	0.14	183.8	178.8
0.3380	27.925	Glacial acetic acid	0.405	114.1	—
0.3412	"	"	0.40	117.1	115.6

##### *β-Methylrhodim*, m. p. 183—184°.

0.094	22.005	Glacial acetic acid	0.110°	151.4	—
0.1604	"	"	0.14	203.0	177.0

##### *isoMethylrhodim*, m. p. 127—128°.

0.1080	19.57	Nitrobenzene	0.105°	378.0	—
0.079	"	"	0.065	404.7	391.35

*Determination of Molecular Weight by the Ebullioscopic Method.*

In alcohol: constant for 100 c.c., 15.6.

Preliminary tests with acetanilide gave an average M.W.=157 instead of 135.

$\alpha$ -Methylrhodim, m. p. 103—104°:0.3312 gram.

Rise in temperature.	Grams in 100 c.c.	M.W.	Average.
0.620°	5.018	126.2	—
0.554	4.476	126.0	—
0.496	4.039	127.0	—
0.440	3.680	130.5	127.4

$\beta$ -Methylrhodim, m. p. 183—184°:0.2175 gram.

0.155°	3.295	331.6	—
0.137	2.939	334.7	—
0.125	2.652	331.0	—
0.110	2.417	342.7	336.66

isoMethylrhodim, m. p. 127—128°:0.1732 gram.

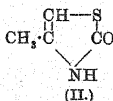
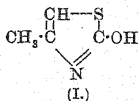
0.078°	2.624	524.8	—
0.070	2.340	522.0	—
0.060	2.112	549.1	—
0.052	1.924	577.2	543.1

$C_4H_5ONS$  requires M.W.=115.

Owing evidently to anomalies of aggregation, the results are not so conclusive as might be desired.  $\alpha$ -Methylrhodim has certainly the simple molecule  $C_4H_5ONS$ , whereas there is some uncertainty concerning the two other isomerides. The author is inclined to regard  $\beta$ -methylrhodim as  $2(C_4H_5ONS)$  and isomethylrhodim as  $4(C_4H_5ONS)$ , the structure of the ring,  $C_4H_5ONS$ , not being necessarily the same in the three isomerides.

*Constitution of the Three Methylrhodims.*

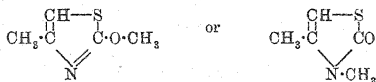
The so-called *meso*-hydroxymethylthiazole has, according to Hantzsch and Weber (*Ber.*, 1887, **20**, 3127), the structural formula I, which is that of a tertiary alcohol or phenol. The only fact



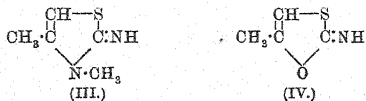
adduced by Hantzsch and Weber in favour of this formula was the alleged formation of *meso*-aminothiazoles by the action of ammonia

or primary bases. Later, however, Hantzsch had to admit the complete indifference of that compound towards ammonia or organic bases, having discovered that the reacting substance was thiocynoacetone alone. This, and similar facts which were gradually evolved in the study of the aminothiazoles, led to these substances being represented as perfect models of tautomerism, hydroxymethylthiazole being endowed with a ketonic double (II), in spite of the absence of properties commonly possessed by ketones, as had been pointed out by Hantzsch and Weber themselves.

The author's long acquaintance with hydroxymethylthiazole has failed to reveal to him a single fact pointing to the presence of either a hydroxyl or a carbonyl group in that compound. It behaves neither as an alcohol nor as a ketone, and it affords no justification whatever for the assumption of tautomerism, that last resort of a formula in difficulties. Furthermore, the action of phosphorus pentachloride, which, as has been shown, leaves the oxygen intact, whilst it introduces chlorine into the molecule, makes the presence of either a hydroxyl or a carbonyl group at least improbable. The two formulæ (I and II) are, however, not only improbable, but impossible, as is proved by the study of the hydrolysis of the methylated derivative,  $\text{CH}_3\cdot\text{C}_4\text{H}_4\text{ONS}$ , which the author has succeeded in obtaining in a state of purity. Indeed, this substance would have to be represented as



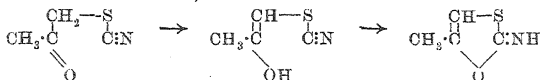
The first of these formulæ is that of an *O*-ether which can give no methylamine on hydrolysis; neither can a substance possessing the second formula, since the  $\text{N}\cdot\text{CH}_3$  group is in the position 3, which, as Traumann (*Annalen*, 1888, **249**, 44) has shown in the case of 2-imino-3:4-dimethyl-2:3-dihydrothiazole (III), yields ammonia on hydrolysis, but no methylamine.



The compound,  $\text{CH}_3\cdot\text{C}_4\text{H}_4\text{ONS}$ , on the contrary, gives a quantitative yield of methylamine.

We are thus led to the conclusion that the group  $\text{N}\cdot\text{CH}_3$  occupies the position 2, which brings us to the formula IV for "hydroxy-

methylthiazole." A compound of this structure may be derived from thiocynoacetone if it is assumed that the latter passes into the enolic form, that a hydrogen atom then migrates, and, finally, that the chain is closed,

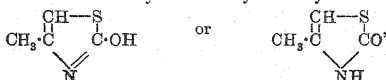


It appears, therefore, that the substance which has been known since 1887 as hydroxymethylthiazole is not a thiazole at all. It might be called 2-imino-4-methylthioxole, but for the sake of simplicity, and in view of the now proved existence of two other isomerides of thiocynoacetone, it seems preferable to adopt the generic name *rhodim* for this class of compounds.

Thus, hydroxymethylthiazole becomes  $\alpha$ -methylrhodim; the isomeride melting at 183—184°,  $\beta$ -methylrhodim; the isomeride melting at 127—128°, *isomethylrhodim*.

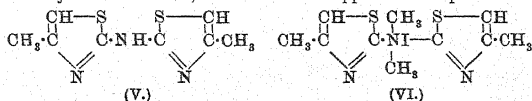
It has been shown that the first two can be easily converted into one another. They stand, therefore, in the closest connexion and have to be considered as structurally analogous, the only difference being in the size of the molecule, that of the  $\beta$ -isomeride being probably double.

The same cannot be said of *isomethylrhodim*; its chemical behaviour, which is quite different, goes to show that it possesses one of the formulæ formerly claimed by  $\alpha$ -methylrhodim,



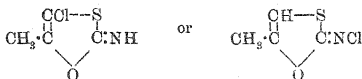
more likely the latter. A glance at it shows pre-existing the fragments,  $\text{CH}_3 \cdot \text{C} : \text{CH} \cdot \text{S}$ ,  $\cdot \text{CO} \cdot \text{NH} \cdot$ , etc., into which the compound can be made to decompose. The formula is, of course, not simple; it would have to be multiplied probably by 4, which could cause it to rank with cyanuric acid, the identity of which with tetracarbamide has been recently demonstrated (Walters and Wise, *J. Amer. Chem. Soc.*, 1917, **39**, 2472).

The base, dithiazylamine,  $\text{C}_3\text{H}_9\text{N}_3\text{S}_2$ , which is formed from *isomethylrhodim* by the action of hydrochloric acid, may be represented by the formula V, which makes it appear as the parent sub-



stance of the ammonium hydriodide,  $C_{10}H_{14}N_3IS_2$ , obtained by Hantzsch and Weber (*Ber.*, 1887, **20**, 3131) in small quantity by the action of methyl iodide on aminomethylthiazole, to which, starting from another direction, they assigned the structural formula VI.

The chlorinated derivative of  $\alpha$ -methylrhodim,  $C_4H_4ONClS$ , may be



more likely the first.

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### XCIH.—An Automatic Extraction Apparatus.

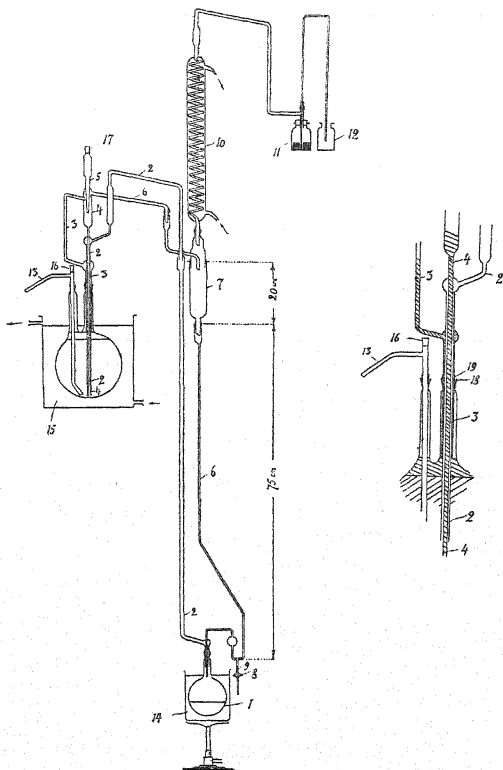
By JOSEPH TCHERNIAC.

THE extraction apparatus described by the author (*Ber.*, 1893, **25**, 3652), and frequently mentioned in the preceding paper, has undergone so many changes in the course of time that it seems desirable to give an account of it in its present shape.

The working of the apparatus is very simple. Of the two flasks shown in the diagram, the smaller one receives the ether and is heated in a water-bath; the large two-necked flask contains the solution to be extracted; it can be filled through the opening (16) of the tube (13), which is also used for siphoning off the exhausted liquor. The capacities of both flasks may vary within very wide limits, from a fraction of a litre to several litres. The two-necked flask is placed in a vessel through which cold water is run; it is then filled nearly to the neck with the liquid to be extracted, the tubes (16 and 13) are closed, and ether is poured in through the opening (17) of the tube (5). The ether flows through the tube (4) to the bottom of the flask, rises in the aqueous liquid and in the annular space between the tubes (3 and 2) (see enlarged inset), and descends through the tubes (6 and 7) into the small flask, filling the seal (9); through the condenser (10) a little mercury is poured to prevent any leakage of ether from the tap (8).

When the water-bath is heated, the vapour of ether raises the liquid ether in the seal to a certain height in the tube (6), and

also passes through the tube (2) to the bottom of the two-necked flask, where it is condensed; the liquid ether then returns through the tubes (3 and 6) and the seal into the small flask. Any aqueous



liquid carried over with the ether returns through the tube (4) into the two-necked flask.

By regulating the flow of water in the vessel (15), the tempera-



ture of the aqueous liquid can either be kept quite low or allowed to rise more or less.

The joints are very simple and efficient. As seen in the sketch (inset), the outer tube is very slightly conical (18), and the inner tube, which is little less in diameter, is provided with a short length of rubber tubing (19), which, on being pressed into the conical opening of the outer tube, makes a perfectly tight joint.

The mercury trap (11 and 12) is connected with the apparatus after the air has been expelled by the vapour of ether; it prevents losses of the solvent by diffusion.

The apparatus may be used equally well for the extraction of solid substances by means of ether, chloroform, etc. In this case, the two-necked flask may be comparatively small, and the tube (7) must be provided with a thimble or filter to arrest any particles of solid that may be carried over by the solvent. The cap of this tube is ground in.

When the apparatus is properly put together and in good order, it may be safely left to work overnight, the requisite condition for its satisfactory working being steady, uniform boiling with entire freedom from all tendency to "bumping." This is secured by the well-known device of introducing into the ether flask small tetrahedra of platinum.

Little ether is lost except that dissolved in the aqueous solution, and if care is taken before extraction to saturate the latter with sodium chloride, the loss of ether is rendered still smaller.\*

In conclusion, I wish to express my thanks to my assistant, Mr. H. A. Steinmann, for the preparation of the excellent diagram of the apparatus which is the subject of this paper.

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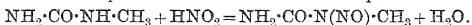
\* The apparatus can be obtained from Messrs. Baird & Tatlock (London) Ltd., 14-15, Cross Street, London, E.C. 1.

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XCIV.—*The Constitution of Carbamides. Part IX. The Interaction of Nitrous Acid and Mono-substituted Ureas. The Preparation of Diazomethane, Diazoethane, Diazo-n-butane, and Diazoisopentane from the Respective Nitrosoureas.*

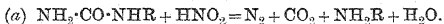
By EMIL ALPHONSE WERNER.

NITROSOMETHYLUREA, obtained by von Brüning (*Ber.*, 1888, **21**, 1809), was the first example of the preparation of a nitroso-derivative from a mono-substituted urea, and its formation has been supposed to take place in accordance with the equation



Later, nitrosophenylurea, and the corresponding *m*- and *p*-tolyl and  $\beta$ -naphthyl derivatives, were prepared by Walther and Wlodkowski (*J. pr. Chem.*, 1899, [ii], **59**, 285).

Assuming the carbamide configuration, it must be admitted that the formation of a nitroso-derivative is rather surprising and requires some explanation, since it would be natural to expect that the amino-group would be at once attacked with complete decomposition of the urea, thus:



Moreover, the yield of nitroso-derivative was not sensibly affected by an addition of an excess of nitrous acid to the substituted urea, nor had nitrous acid any further action on the nitroso-compound when once formed. The latter, therefore, could not contain an amino-group.

A quantitative study of the changes involved has brought to light some interesting facts bearing on the question of the constitution of mono-substituted ureas, whilst the nitroso-derivatives examined are of more than ordinary interest, since they are likely to prove most useful substances for the simple preparation, and study, of the reactions of diazomethane and its homologues.

When methylurea in aqueous solution (*N*/5) was treated with nitrous acid in the presence of sulphuric acid, there was an immediate violent evolution of nitrogen and carbon dioxide, which ceased after a few seconds. This was quickly followed by the separation of crystals of a nitroso-derivative, the yield of which was, in round numbers, equal to 90 per cent. of the theoretical (Expts. 1 and 2).

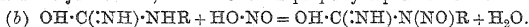
In the case of ethyl-, *n*-butyl-, and *iso*amyl-urea, whilst similar

phenomena were observed, the yields of the respective nitroso-derivatives were approximately 76, 67, and 48 per cent. of the theoretical.

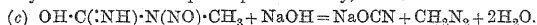
With benzylurea and phenylurea, respectively, where it was necessary to use a relatively large proportion of pure acetic acid to effect solution, 42 and 33 per cent. of the theoretical proportions of the nitroso-derivatives were formed.

The remainder of the respective ureas was decomposed according to equation (a), as proved by the evolution of larger volumes of carbon dioxide and nitrogen in proportion to the lower yields of nitroso-derivatives, and since the velocity of reaction (a) was greater than that which gave rise to the latter compounds, the evidence goes to show that the proportions of each substituted urea present in solution with a true "carbamic" structure must be different.

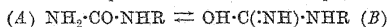
In connexion with this point, it is important to note that the tendency to form a nitroso-derivative falls as the electropositive character of the hydrocarbon radicle diminishes. In the light of the facts just stated, this reaction is properly represented thus:



An outstanding property of the aliphatic nitroso-derivatives is their immediate decomposition by alkalis, which in the case of the methyl derivative takes place quantitatively, as follows:

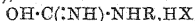


This change,\* together with several other reactions described in the experimental part, supports the above constitution. It follows, therefore, that, so far as their behaviour towards nitrous acid is concerned, mono-substituted ureas in acid (sulphuric, hydrochloric, or nitric) solution are present in two forms in equilibrium, thus:



the proportion of each form being regulated by the electrochemical nature of the radicle (R).

Methylurea, for example, must be very largely presented for attack in the form (B), the formation of a salt of the type



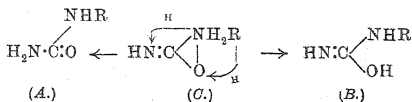
being promoted by the presence of the strongly electropositive methyl group. Phenylurea, on the other hand, is mainly present in the form (A), since the tendency to salt-formation is here distinctly feeble.

\* The ~~secondary~~ reaction, resulting from the decomposition of diazomethane by water, is not considered here, and is dealt with later. In the case of the ethyl, *n*-butyl, and isocamyl compounds, some olefines are produced along with the diazo-derivative.

Further evidence in favour of the above view was found in the fact that mono-substituted ureas were directly attacked by nitrous acid in solution alone, even at a concentration of  $N/18$ , and whilst the velocity of the reaction at this low concentration was bound to be slow, it was quite appreciably promoted by the presence of a weak acid, such as acetic, particularly at concentration  $N/5$  (Expt. 3).

In this respect, the substituted ureas differed markedly from urea itself (compare T., 1914, 111, 864), and whilst the velocity of the reaction was slow, the end result was much the same as in the presence of a strong acid.

The probable existence of a cyclic form of the urea capable of giving rise to either forms (A) or (B) by migration of hydrogen, thus:



must be taken into consideration as a likely condition in a neutral solvent or in the presence of a weak acid. The diminished velocity in the reaction with nitrous acid under such conditions becomes intelligible, since form (C), like urea itself, would not be attacked by the reagent. Whilst the behaviour of di- and tri-substituted ureas towards nitrous acid is under investigation, it may be mentioned here that nitrosodiethylurea,  $\text{NHEt}\cdot\text{CO}\cdot\text{NEt}\cdot\text{NO}$ , readily furnished diazoethane on treatment with either sodium hydroxide or sodium ethoxide.

## EXPERIMENTAL.

### *Interaction of Nitrous Acid and Methylurea. Preparation and Properties of Nitrosomethylurea.*

All the gasometric experiments described were performed in a Lunge nitrometer, and, for the sake of brevity, only the volumes corrected to  $N.T.P.$  are given in each case.

*Expt. 1.*—0.074 Gram of methylurea and 0.072\* gram of sodium nitrite (equal molecular proportions) were dissolved in 3 c.c. of water, and 2 c.c. of  $N$ -sulphuric acid added. The concentration was  $N/5$ . After one minute, there was sudden separation of crystals (the nitroso-derivative), and the evolution of gas at once ceased.

\* The equivalent of 0.069 gram of pure sodium nitrite.

Vol. of  $N_2 = 2.3$  c.c. = 10.26 per cent. of the theoretical for equation (a). Theory = 22.4 c.c.  $N_2$ .

The gas was expelled from the nitrometer, and 2 c.c. of 15 per cent. potassium hydroxide solution were added to the residue. There was instant violent evolution of gas of a deep yellow colour ( $CH_3N_2$ ), which gradually became colourless after remaining over the aqueous solution for some time.

Vol. of  $N_2 = 20.12$  c.c. = 89.82 per cent. of the theoretical for the formation of the nitroso-derivative according to equation (b). Theory = 22.4 c.c.  $N_2$ .

*Expt. 2.*—0.074 Gram of methylurea and 0.144 gram of sodium nitrite were dissolved in 2 c.c. of water ( $HNO_2$  to methylurea = 2:1), and 3 c.c. of *N*-sulphuric acid added.

Vol. of  $N_2 = 2.4$  c.c. = 10.71 per cent. of the theoretical.

After addition of potassium hydroxide solution to the residue, vol. of  $N_2 = 19.95$  c.c. = 89.06 per cent. of the theoretical for the nitroso-derivative, the yield of which was therefore unaffected by an excess of nitrous acid.

*Expt. 3.*—0.074 Gram of methylurea and 0.072 gram of sodium nitrite were dissolved in 17 c.c. of water, and 1 c.c. of *N*-sulphuric acid was added. The concentration was *N*/18, and no free sulphuric acid was present. The evolution of gas was very slow, and at the end of twenty hours vol. of  $N_2 = 1.6$  c.c. = 7.14 per cent. of the theoretical.

Vol. of  $N_2 = 17.88$  c.c. (after addition of potassium hydroxide) = 79.82 per cent. of the nitroso-derivative formed.

Whilst the reaction in this case was not completed after twenty hours, the results prove that methylurea is directly attacked by nitrous acid alone on the same lines as in the presence of a strong acid. When an excess of acetic acid was present, the reaction was completed in about ten hours with results similar to those described in Expts. 1 and 2.

The following procedure was found most suitable for the preparation of nitrosomethylurea on a larger scale.

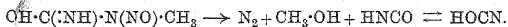
Methylurea (44.4 grams) and sodium nitrite (43.2 grams) were dissolved in 400 c.c. of water contained in a wide-mouthed bottle of 1200 c.c. capacity partly immersed in ice-cold water. A cold solution of 30 grams of pure sulphuric acid in 150 c.c. of water was gradually added, the liquid being well stirred. After two hours, the nitroso-derivative, which had separated, was collected, washed, and dried in a desiccator; it weighed 49.4 grams. The filtrate (and washings) was extracted twice with 80 c.c. of ether, from which solvent, after distillation at a gentle heat, 2.2 grams of the nitroso-compound were obtained. Total yield = 51.6 grams, or

83.5 per cent. of the theoretical. On account of the vigorous evolution of gas and the simultaneous separation in microcrystalline form of the nitroso-compound, the latter was almost entirely carried to the surface as a thick froth; for this reason, the use of a flask should be avoided.

When sulphuric acid was replaced by about twice its equivalent of pure acetic acid in the above preparation, the nitroso-compound separated in highly refractive, tetragonal prisms, there was much less frothing, but it was necessary to allow the preparation to continue for not less than twenty-four hours before the maximum yield was attained, which even then was about 10 per cent. less than when sulphuric acid was used. Whilst individual crystals of nitrosomethylurea appear quite colourless, in bulk the compound has a pale buff colour rather than yellow, as described by von Brüning (*loc. cit.*). The crystals are readily soluble in alcohol, acetone, or ether, moderately so in benzene or chloroform, and almost insoluble in cold water.

On exposure to sunlight, the compound gradually loses its buff colour and becomes pale sea-green; beyond a fall in the melting point, this change had no apparent effect on the general reactions of the substance.

When an alcoholic solution of nitrosomethylurea was heated to the boiling point, it was gradually decomposed, thus:



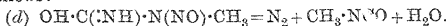
Ethyl allophanate was produced as a result of the interaction of cyanic acid and ethyl alcohol.

In connexion with this decomposition, a curious difference was found in the stability of specimens of nitrosomethylurea prepared in the presence of sulphuric acid and of acetic acid respectively.

*Expt. 4.*—(a) A solution of 5 grams of nitrosomethylurea (acetic acid preparation) in 70 c.c. of alcohol was boiled under reflux; the buff-yellow colour of the solution gradually disappeared, and, after two hours, the solution was colourless. On cooling, ethyl allophanate, identified by its melting point (191°) and properties, separated, and the amount ultimately obtained was 2.28 grams, or 1.24 per cent. of the theoretical (theory = 3.2 grams from 5 grams of nitrosomethylurea). (b) A similar experiment with a specimen prepared in sulphuric acid solution gave, after two hours, 27.4 per cent., and after three hours only 40.94 per cent. of the theoretical yield of ethyl allophanate. For the present, no explanation can be offered for this apparent anomaly, which has been verified with several specimens.

Nitrosomethylurea melted at 121° (crystals from ether), and in

contrast to the foregoing change was violently decomposed, as follows:



Most of the isocyanic ester was obtained as the polymeride,  $(\text{CH}_3 \cdot \text{NCO})_3$ , which melted at  $177^\circ$  (Hofmann gives  $176^\circ$ ).

*Preparation of Diazomethane from Nitrosomethylurea.*

In order to obtain the best yield of diazomethane in solution in ether, either of the following methods can be recommended.

*Expt. 5.*—Nitrosomethylurea (10.3 grams) in microcrystalline form was introduced into a round-bottomed flask of about 100 c.c. capacity, 50 c.c. of pure ether (distilled over sodium) were poured down the side of the flask, which stood in melting ice, and, without delay, 20 c.c. of 70 per cent. potassium hydroxide solution were quickly added drop by drop, while a quiet, circular motion was given to the flask. After about ten minutes, the deep golden-yellow, ethereal solution was decanted. It contained 3.2 grams of diazomethane, determined by the iodine method, which was equal to 76.2 per cent. of the theoretical for equation (c).

Whilst it was not possible to avoid decomposition of a considerable proportion of diazomethane by the water generated during the reaction, the effect was slightly reduced by altering the order of procedure; thus, when nitrosomethylurea was added in portions of about 0.5 gram at a time to very concentrated potassium hydroxide solution lying under the surface of ether, a solution of diazomethane was obtained which contained 78—79 per cent. of the theoretical.

In studying the use of diazomethane as a methylating agent, it has been apparently the universal practice to employ the substance exclusively in ethereal solution. This has obviously a serious disadvantage, on account of the limitations of ether as a solvent for many types of organic compounds. There seems no reason why this practice should be so rigidly adhered to, as shown by the following experiments.

*Expt. 6.*—To a solution of 1.03 grams of nitrosomethylurea in 40 c.c. of pure alcohol, a molecular proportion of sodium ethoxide in 10 c.c. of alcohol was added. Sodium cyanate was immediately precipitated, accompanied by a quiet evolution of nitrogen, which ceased at the end of about fifteen minutes, and a rich yellow solution of diazomethane was obtained. To 5 c.c. of the solution placed in the nitrometer, 10 c.c. of water were added; there was immediate brisk evolution of nitrogen, while the liquid became colourless.

Vol. of  $\text{N}_2$  (measured over water) = 17.91 c.c. Hence for total

solution = 179.1 c.c. Theory = 224 c.c. Therefore the solution contained 79.9 per cent. of the theoretical proportion of diazomethane.

*Expt. 7.*—A solution of 0.103 gram of nitrosomethylurea in 3 c.c. of alcohol was introduced into the nitrometer, and 0.068 gram of sodium ethoxide in 2 c.c. of alcohol was added.

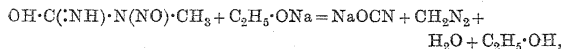
After twenty hours, only 4.5 c.c. of nitrogen (corrected for pressure of alcohol vapour) were evolved.

The gas was expelled from the nitrometer, and 10 c.c. of water were added, when there was immediate rapid evolution of nitrogen.

Vol. of  $N_2$  = 16.84 c.c. (Theory = 22.4 c.c.)

The solution therefore contained, after remaining for twenty hours, 75.3 per cent. of the theoretical amount of diazomethane.

It will be seen from the equation,



that whilst the amount of water produced was theoretically capable of decomposing all the diazomethane formed, its effect was greatly suppressed by the presence of a relatively large volume of alcohol. It may be mentioned that results very similar to those recorded in *Expt. 7* were obtained when diazomethane was generated in the presence of pure methyl, propyl, *n*-butyl, and *iso*amyl alcohol respectively. Moreover, since there was no evidence of the formation of an ether ( $R \cdot O \cdot CH_3$ ), it must be concluded that diazomethane does not attack the hydroxyl group of an alcohol.

The chief point of practical interest arising out of these observations lies in the simple application of the reaction as a method for studying the properties of diazomethane under more favourable conditions. In the case of a neutral substance, for example, it may be dissolved in alcohol,\* together with a small excess of nitrosomethylurea; on addition of the requisite amount of sodium ethoxide, diazomethane is instantly generated *in situ* with the substance to be attacked.

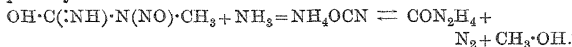
#### *Decomposition of Nitrosomethylurea by Ammonia.*

When an alcoholic solution of ammonia was added to a similar solution of nitrosomethylurea cooled to  $0^\circ$ , there was vigorous evolution of nitrogen, and a colourless solution was obtained. After a few minutes, a certain quantity of acicular prisms separated, which were identified as ammonium cyanate. As the

\* Pure alcohol which has been finally dried by adding to it a small quantity of an ethereal solution of diazomethane may be used with advantage.



temperature was allowed to rise, the crystals redissolved. The primary reaction was as follows:



Three experiments gave yields of urea which varied from 42 to 53 per cent. of the theoretical. Methylurea and a small quantity of *as*-dimethylurea (which melted at 181°) were separated from the mother liquors; these were the result of (1) the methylation of ammonia,  $\text{CH}_2\text{N}_2 + \text{NH}_3 = \text{CH}_3\cdot\text{NH}_2 + \text{N}_2$ , and (2) the further methylation of methylamine to dimethylamine. As the reaction progressed, each amine decomposed a portion of nitrosomethylurea according to the above equation. The further study of these reactions will form the subject of a future communication.

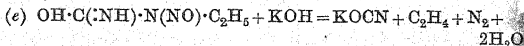
*The Spontaneous Decomposition of Nitrosomethylurea.*

It may be worth while to point out that no specimen of nitrosomethylurea could be kept unchanged for more than about five months. One preparation (about 30 grams), stocked in a dark brown, glass-stoppered bottle, decomposed spontaneously after 162 days, although only three days previously several grams removed for the preparation of diazomethane behaved in a normal manner. The decomposition was on the lines of the change produced by heat (equation *d*), and whilst much trimethyl *isocyanurate* was formed, a viscous product freely soluble in water was generated, the nature of which has not yet been elucidated.

The behaviour of a number of other substituted ureas towards nitrous acid is shown below. The experiments were carried out as described under Expt. 1.

	Vol. of N <sub>2</sub> evolved. C.c.	Decomposition according to equation (a). Per cent.	Yield of nitroso- derivative. Per cent.
1. Ethylurea .....	5.3	23.66	76.34
2. <i>n</i> -Butylurea.....	7.99	32.60	67.40
3. <i>iso</i> Amylurea .....	11.5	51.33	48.67
4. Benzylurea .....	12.97	57.90	42.10
5. Phenylurea .....	14.96	66.78	33.22

Nitrosoethylurea, prepared in a manner similar to the methyl derivative, was obtained in pale buff-yellow, hexagonal plates which melted at 103—104°. Diazoethane was obtained on decomposition with potassium hydroxide according to equation (c); ethylene to the extent of 14.77 per cent. of the theoretical was simultaneously formed, thus:



A very good yield of diazoethane in ethereal solution was readily prepared by the method described under Expt. 5.

*Nitroso-n-butylurea*,\*  $C_5H_{11}O_2N_3$ , formed almost colourless, hexagonal plates which melted at  $85^\circ$ . Diazo-*n*-butane was obtained as an amber-coloured, mobile liquid with a stupefying odour by the direct addition of nitrosobutylurea to 70 per cent. potassium hydroxide solution cooled to  $0^\circ$ ; butylene and nitrogen were simultaneously formed to the extent of about 30 per cent. of the theoretical on the lines of equation (e).

*Nitrosoisoamylurea*,  $C_6H_{13}O_2N_3$ , was obtained in minute, pale buff, unctuous, platy crystals which melted at  $74^\circ$ ; since *isoamylurea* is sparingly soluble in water, it was necessary to use 30 per cent. acetic acid as solvent in the preparation of the nitroso-derivative.

*Diazoisopentane*,  $C_5H_{10}N_2$ , was obtained as a dark brown oil of unpleasant odour by the addition of potassium hydroxide solution to the nitroso-urea.

*Nitrosobenzylurea*,  $C_8H_9O_2N_3$ , which was prepared by the action of nitrous acid on benzylurea dissolved in 50 per cent. acetic acid, formed many-sided prisms which melted at  $101^\circ$ ; these were insoluble in water, but readily soluble in alcohol or ether.

Phenyldiazomethane,  $C_6H_5 \cdot CH:N_2$ , separated as a deep reddish-brown oil on the addition of the nitroso-compound to a 70 per cent. solution of potassium hydroxide.

### Summary.

(1) The interaction of mono-substituted ureas and nitrous acid in two directions, with (a) production of nitroso-derivatives, and (b) the complete disruption of the molecule, is explained by the presence in solution of two structural forms of the urea in equilibrium.

(2)  $\bar{P}$  nitroso-derivatives are shown to have the constitution  $OH \cdot C(\bar{N}_2) \cdot N(NO)R$ , and their formation is promoted in proportion to the electropositive character of the radicle (R) in the original urea.

(3) The aliphatic nitroso-derivatives are decomposed by alkalis with the production of diazo-derivatives of the paraffins in very good yields.

\* *n*-Butylurea,  $C_5H_{12}ON_2$ , from which the nitroso-derivative was obtained has not been hitherto described. It was readily obtained by evaporating at  $100^\circ$  an aqueous solution of *n*-butylamine hydrochloride and potassium cyanate. It formed crystals which melted at  $86^\circ$  and were readily soluble in water or alcohol.

(4) It is shown that diazomethane and its homologues may be conveniently prepared in alcoholic solution for the study of their reactions.

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[Received, July 11th, 1919.]

### XCV.—*Dyes Derived from Quinolinic Acid.*

By PRAPHULLA CHANDRA GHOSH.

THE object of the present investigation was to prepare dyes from quinolinic acid analogous to the phthaleins, and to compare their colour and fluorescence. That quinolinic acid condenses with phenol and resorcinol has, indeed, been mentioned by Noelting and Collin (*Ber.*, 1884, **17**, 258), but few details were given, and the products were not analysed. A compound from quinolinic acid and hydroxyquinol has been described by Liebermann and Wölbling (*Ber.*, 1902, **35**, 1786). In the present work, the condensation of quinolinic acid with resorcinol, catechol, phloroglucinol, *m*-phenylenediamine, *m*-dimethylaminophenol, and 2:4-diaminophenol has been effected. These condensations take place without the use of any condensing agent by simply heating the two constituents together.

In comparison with the corresponding phthaleins, the effect of the presence of the nitrogen atom in the ring is to lighten the colour and to diminish the fluorescence. In this series of compounds, the greater the power of an auxochromic group to deepen the colour, the greater is its effect on fluorescence. The compound obtained from quinolinic acid and *m*-dimethylaminophenol has the deepest colour and is the most strongly fluorescent.

Dyes analogous to hydroxyanthraquinones have not yet been prepared, but work in this direction is being continued.

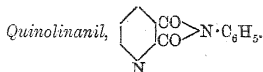
#### EXPERIMENTAL.

Quinolinic acid was prepared by oxidising a solution of quinoline (10 grams) in acetone (150 c.c.) with a 5 per cent. aqueous solution of the theoretical quantity of potassium permanganate at about 10°.

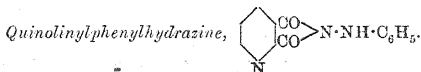
If the manganese dioxide is dried in the air, powdered, and then extracted with alcohol, the solution, on concentration, deposits pale yellow needles melting at 71—72°. This substance is insoluble in

alkali hydroxides and volatile with steam. The amount obtained was sufficient only for an estimation of nitrogen:

0.1145 gave 17.6 c.c.  $N_2$  at  $31^\circ$  and 756 mm.  $N=17.16$  per cent.



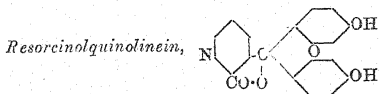
Half a gram of quinolinic acid and 2 c.c. of aniline were heated on the sand-bath for ten to fifteen minutes, when the whole of the acid dissolved. On cooling, crystals separated, which were collected and washed with alcohol. They formed colourless, prismatic needles melting at  $248-251^\circ$  (Engler, *Ber.*, 1894, **27**, 1789, gives  $228^\circ$ ) (Found:  $N=13.4$ .  $C_{13}H_8O_2N_2$  requires  $N=12.50$  per cent.).



Half a gram of the acid was heated with 2 c.c. of phenylhydrazine for about ten minutes. The clear solution, on cooling, became syrupy, and on adding alcohol, crystals were obtained which, when collected and washed free from phenylhydrazine, melted and decomposed at  $237-238^\circ$ :

0.099 gave 15.9 c.c.  $N_2$  at  $31^\circ$  and 755 mm.  $N=17.68$ .

$C_{13}H_8O_2N_3$  requires  $N=17.55$  per cent.



Two grams of quinolinic acid and 4 grams of resorcinol were heated at  $180-200^\circ$  for two hours. Some violet colouring matter sublimed, which might have been due to the formation of a substance resembling 1:3-dihydroxyanthraquinone. On cooling, the fusion was extracted with alcohol, and the dye was precipitated from the alcoholic extract with water. It could not be crystallised. It melts and decomposes at  $266-267^\circ$ . It is fluorescent in alcohol, acetone, or toluene, and aqueous potassium hydroxide gives an orange-green fluorescence:

0.1020 gave 0.2550  $CO_2$  and 0.032  $H_2O$ .  $C=68.1$ ;  $H=3.48$ .

$C_{19}H_{11}O_5N$  requires  $C=68.46$ ;  $H=3.33$  per cent.

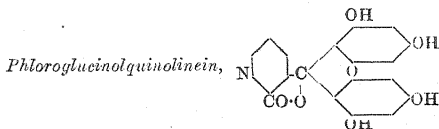
The *silver* salt was prepared in the ordinary way:

0.2132 gave 0.1092 AgCl. Ag = 38.6.

$C_{19}H_9O_5NaAg_2$  requires Ag = 39.5 per cent.

*Catecholquinolinein.*

This compound has not yet been obtained in sufficient quantity for analysis. It is prepared and purified in the same way as the above compound. It dissolves in aqueous potassium hydroxide with a greenish-blue colour.



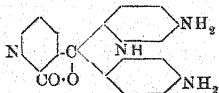
Two grams of quinolinic acid and 4 grams of phloroglucinol were heated at 130—150° for about ten minutes. At first the mixture melted, the colour changing to red, and then the whole solidified. On crystallisation from water, a red compound melting and decomposing at 275—277° was obtained, which was very readily soluble in alcohol:

0.100 gave 0.2277  $CO_2$  and 0.0289  $H_2O$ . C = 62.1; H = 3.21.

$C_{19}H_{11}O_7N$  requires C = 62.46; H = 3.01 per cent.

If the solid mass is dissolved in alcohol and the solution concentrated, a pale yellow, crystalline compound is obtained which does not melt at 295°. It dissolves in aqueous potassium hydroxide with a yellow colour like the hydroxybenzophenones, and is more readily soluble in water than the compound just described. It has not been obtained in sufficient quantity for analysis.

*m-Phenylenediaminequinolinein,*

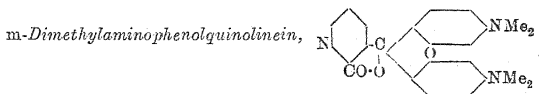


One gram of quinolinic acid and 3 grams of *m*-phenylenediamine hydrochloride were heated slowly to 210° and kept at 210—220° for twenty to twenty-five minutes. After cooling, the mass was extracted with alcohol and filtered; the solution was fluorescent.

The dye was obtained in a pure state by adding ether to the alcoholic solution. It melts and decomposes at 232—235°:

0.103 gave 15.4 c.c.  $N_2$  at 30° and 758 mm.  $N=16.73$ .

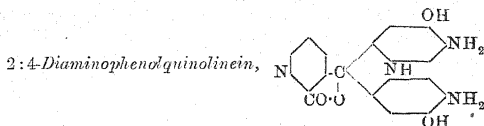
$C_{19}H_{14}O_2N_4$  requires  $N=16.97$  per cent.



Quinolinic acid (0.75 gram) and *m*-dimethylaminophenol (1.5 grams) were heated at 120—130° for fifteen to twenty minutes, and then the temperature was slowly raised to 150°, when heating was stopped. The mass was extracted with alcohol, and the dye precipitated from the solution with water. When crystallised from dilute alcohol, it melted and decomposed at 148—151°. The alcoholic solution shows a reddish-violet fluorescence, which is deeper in acetic acid or alcoholic hydrochloric acid:

0.1062 gave 10.8 c.c.  $N_2$  at 32° and 751.4 mm.  $N=11.1$ .

$C_{21}H_{21}O_3N_3$  requires  $N=11.5$  per cent.



One gram of quinolinic acid and 3 grams of 2:4-diaminophenol hydrochloride were slowly heated to 180° and kept at this point for a few minutes. The dye was extracted by boiling with alcohol and filtering from the unchanged diaminophenol hydrochloride. It was purified by dissolving in alcohol and precipitating with water, but could not be crystallised. It does not melt at 290°. The compound is reddish-brown, and its solution in alcohol is fluorescent:

0.101 gave 13.8 c.c.  $N_2$  at 30° and 756 mm.  $N=15.37$ .

$C_{19}H_{14}O_4N_4$  requires  $N=15.47$  per cent.

In conclusion, I beg to express my great indebtedness to Sir P. C. Rây for the loan of 200 grams of quinoline.

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[Received, July 31st, 1919.]

XCVI.—*Sodium Hypochlorite.*

By MALCOLM PERCIVAL APPLEBEY.

SODIUM HYPOCHLORITE in a solid form was first obtained by Muspratt and Shrapnell Smith, of the United Alkali Co., Ltd., in the course of investigations directed towards the preparation of very concentrated solutions (*J. Soc. Chem. Ind.*, 1898, 17, 1096; 1899, 18, 210; 1903, 22, 591). Their preparations were obtained by cooling concentrated solutions, and had a composition corresponding approximately with a hexahydrate. The product melted in its water of crystallisation at  $20^{\circ}$ , and the fusion was unstable. It could be dehydrated slowly by means of a current of dry air under diminished pressure, and had then a melting point of  $45^{\circ}$ , but the results were deemed to be of no commercial value, and the investigations were accordingly discontinued.

It was suggested by Mr. Muspratt that a complete investigation of the hydration and solubility relationships might furnish information of both scientific and industrial value, and a preliminary survey of the field has accordingly been made. This has already yielded results of some importance, which are the subject of this communication. They are to be regarded as provisional, and will be followed at a later date by a systematic phase-rule treatment.

*Preparation and Properties of Muspratt's Hydrate.*

The hypochlorite solutions were prepared by treating 35 per cent. sodium hydroxide solution cooled in ice-water with chlorine, removing the precipitated sodium chloride, adding sodium hydroxide equivalent to the sodium chloride separated, and repeating the treatment with chlorine until the solution was about 5*N* when tested with neutral sodium arsenite solution. On a few occasions, preparations were lost owing to spontaneous transformation to chlorate and chloride. Such transformation, when it sets in, takes place with extreme rapidity in concentrated solutions, and is accompanied by the evolution of considerable quantities of gas consisting of both chlorine and oxygen. The transformation to chlorate can, however, be prevented by observing the three conditions laid down by Muspratt and Shrapnell Smith, namely, (1) low temperature; (2) absence of iron or other heavy metals which act as catalysts; (3) presence of excess of free alkali. The solution, which has been freed from precipitated sodium chloride, is

now cooled to about  $-10^{\circ}$  in a freezing mixture and induced to crystallise, either by shaking or by impregnating with a crystal from a previous preparation. The hypochlorite then separates as a mass of very fine, hair-like crystals filling the whole liquid, whilst the temperature rises considerably. When the whole has again reached the temperature of the freezing mixture, the crystals are separated from the mother liquor by suction through a Büchner funnel without filter paper or asbestos, the form of the crystals being such as to make their retention easy. The crystals are pressed down to remove adhering mother liquor, and then appear to be colourless at the top, although the mass in the lower part of the funnel is green, owing to the presence of mother liquor, which cannot be entirely removed, being formed anew by deliquescence during filtration. The crystals liquefy at temperatures varying between  $18^{\circ}$  and  $19^{\circ}$ , according to their purity. The fusion is not quite transparent, but becomes so at a somewhat higher temperature. This behaviour, in conjunction with the subsequent separation of a lower hydrate on cooling, appears to show that the hydrate does not melt completely, but undergoes a transformation at about  $19^{\circ}$  to a lower hydrate, formed in very small quantity, and its saturated solution, which has almost the same composition as the original crystals.

Analysis of the crystals gave somewhat unsatisfactory results, since, owing to the low melting point and rapid deliquescence, it was difficult to secure a sample in a sufficiently dry state. After several trials, it was found best to filter off a small quantity in a Gooch crucible without asbestos, and to break up the crystals in the crucible with a spatula while the suction continued. All attempts to dry the crystals with filter paper failed, owing to the rapid oxidising action on the paper, which resulted in the development of heat, and after a time led actually to charring of the paper. For analysis, the substance was weighed out and dissolved in water, and aliquot parts of the solution were titrated against arsenite for active chlorine and against silver nitrate and thiocyanate for total chlorine after reduction of the hypochlorite with the correct amount of arsenite solution. The following analytical data refer to two specimens which gave for total chlorine quantities not greater than would be formed from the hypochlorite present, and were therefore free from chloride:

Sample I, prepared by twice recrystallising after fusion:

1.1147 gave active chlorine  $0.4065 = 36.47$ .

$\text{H}_2\text{O}$  (by difference)  $0.6899 = 62.07$ .



Sample II, prepared by synthesis from the pentahydrate:

0.5020 gave active chlorine  $0.1807 = 35.99$ .

$H_2O$  (by difference)  $0.3123 = 62.21$ .

$NaOCl, 7H_2O$  requires active chlorine  $= 35.36$ .  $H_2O = 62.88$  per cent.

$NaOCl, 6H_2O$  requires active chlorine  $= 38.85$ .  $H_2O = 59.21$  per cent.

From these data, it would appear that Muspratt's hydrate is nearer in composition to a heptahydrate than to a hexahydrate. At the same time, the agreement with the heptahydrate formula is by no means good, and it may be found on further investigation that more than one hydrate is present in the crystals prepared by Muspratt's method.

#### *Sodium Hypochlorite Pentahydrate.*

When the cloudy liquid obtained by heating the heptahydrate to  $20^\circ$  is allowed to cool slowly to the ordinary temperature, large and well-formed crystals of a new hydrate are obtained. The crystals are greenish-yellow, and contain a considerable amount of mother liquor; when they are broken up in an agate mortar, a separation of liquid takes place, and the powdered substance must be freed from this liquid by filtration through a Gooch crucible.

When prepared in this way, the substance gave the following analytical results:

	I.	II.	Calculated for $NaOCl, 5H_2O$ .
Weight of substance .....	0.3482 gram	0.3786 gram	—
Active chlorine .....	0.1473 "	0.1615 "	—
" " per cent. ...	42.32	42.66	43.10
Cl as chloride .....	0.0006	nil	—
Water (by difference) .....	0.1929 gram	0.2090 gram	—
" " per cent. ....	55.40	55.20	54.75
Loss on heating .....	63.51	—	64.47

The pentahydrate melts at  $27^\circ$ , and is thus a much more practicable substance than the heptahydrate. The fusion is in this case also somewhat cloudy, but the nature of the suspension cannot yet be definitely stated. Up to the present, a small amount of decomposition has always taken place during melting. The pentahydrate is very deliquescent, but the crystals are not unstable at the ordinary temperature if kept in a well-stoppered bottle; a specimen kept for more than a week in a corked test-tube in a well-lighted laboratory showed no measurable increase in chloride content, although some deliquescence had taken place.

The mother liquor from which the pentahydrate has separated

may be made to give a further yield of pentahydrate by freezing out heptahydrate, heating the latter to  $20^{\circ}$ , and allowing to crystallise as before. By this procedure, there is no difficulty in converting at least 50 per cent. of the heptahydrate into the corresponding amount of pentahydrate.

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[Received, August 6th, 1919.]

## XCVII.—Capsaicin. Part I.

By ARTHUR LAPWORTH and FRANK ALBERT ROYLE.

CAPSAICIN, the pungent principle of the fruit of various species of the genus *Capsicum*, was first isolated in crystalline form by Thresh (*Pharm. J.*, 1876, [iii], 7, 21, 259, 473; 1877, 8, 187) and assigned by him the formula  $C_9H_{14}O_2$ . Micko (*Zeitsch. Nahr. Genussm.*, 1898, 818) showed that the substance contained nitrogen, and as a result of analyses and molecular-weight determinations deduced the formula  $C_{18}H_{25}O_3N$ .

Thresh showed that capsaicin is a phenol, but did not discover any other very marked chemical characters; Micko, whose contributions are probably of most importance amongst those of subsequent investigators, established the fact that the molecule of capsaicin contains one phenolic hydroxyl group and one methoxyl group, and this, on the basis of his empirical formula, leads to the expression  $C_{17}H_{24}ON(OH)(O\cdot CH_3)$  for the substance. Micko prepared the indifferent benzoyl derivative and observed that under certain conditions capsaicin undergoes slight decomposition, emitting a faint odour reminiscent of vanillin.

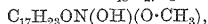
A comprehensive bibliography of the subject is given in Thorpe's "Dictionary of Applied Chemistry" (1913, 4, 559).

The present authors began the investigation of the subject in 1914, at which time the only significant data bearing on the chemical nature and structure of capsaicin were the facts above cited. Their study was greatly retarded by other work arising out of the war, and in view of this fact, and especially as the active interest in compounds with pungent characters has been manifested in countries where scientific research has had no such serious setback as here, it is thought desirable to place on record the progress which has now been made.

The authors have examined various methods previously used for isolating pure capsaicin from the crude extract made from the seeds

and have worked out a process which combines a number of devices some of which are based on details of the processes suggested by previous workers, but as a whole appears especially simple in practice.

The properties of capsaicin which have been described by Thresh, Micko, and by Nelson (*Chem. News*, 1911, **103**, 111) have been confirmed in all essential details, but the analyses made have consistently pointed to the formula  $C_{18}H_{27}O_3N$  or



and not that proposed by Micko, which contains one more atom of hydrogen and is inconsistent with the normal valencies of these four elements in carbon compounds.

The methyl derivative,  $C_{17}H_{23}ON(O\cdot CH_3)_2$ , hereafter termed methylcapsaicin, has been prepared and characterised; it is non-phenolic and is much less pungent than the parent substance.

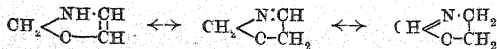
Both capsaicin and methylcapsaicin are feebly basic. They are extremely stable towards hot concentrated alkali hydroxides, but are very slowly attacked by hot acids; the products of hydrolysis have not been determined, but ammonia is always one of them, methylamine being entirely absent. The action of phosphorus pentachloride on methylcapsaicin yields a small quantity of a volatile, nitrogenous oil; this the authors suspect to be the nitrile of a fatty acid, but have not yet had the opportunity of examining it closely.

Most attention has been paid, in the first instance, to the action of reducing agents, many of which evidently attacked capsaicin to a certain extent (as was evidenced by the ready formation of ammonia or ammonium salts), without any obvious general destruction or charring.

From the more highly purified capsaicin, reduced by means of sodium and ethyl alcohol, ammonia was obtained and also, among other products, a small quantity of a compound, the bulk of which boiled at about  $216-217^\circ$  and had the odour and general properties of a fatty alcohol.

Oxidation of methylcapsaicin takes place readily, and among other products veratric acid,  $C_6H_3(OMe)_2\cdot CO_2H$ , was the most readily recognised. There was also formed a fatty acid, of which scarcely sufficient was obtained to identify with complete certainty.

Even disregarding such of the above considerations as are yet not fully substantiated, it is probable that capsaicin is a *C*-disubstituted derivative of one of the isodynamic forms of dihydro-oxazole:



## EXPERIMENTAL.

*Isolation of Capsaicin.*

The ordinary alcoholic extract of capsicums consists mainly of gum or dextrin-like compounds, soluble in water, together with substances which have the characters of saturated and unsaturated carboxylic acids, and relatively small amounts of fats.

In order to isolate capsaicin from this mixture advantage is taken of the fact that capsaicin does not form a stable barium salt when it is brought into contact with aqueous barium chloride which has been rendered ammoniacal. In the same circumstances, however, the free carboxylic acids present in the extract are mainly precipitated as barium salts which are for the most part insoluble in water, alcohol, or ether, or, more especially, in acetone. The gum-like substance present remains dissolved in the water, which retains only traces of capsaicin easily recovered by extraction with ether, and the bulk of the active principle, together with the fats, is found in the precipitate. On extraction of the precipitate with alcohol or ether the capsaicin and fats dissolve, whilst the bulk of the barium salts are insoluble. These operations, by eliminating the dextrin and fatty acids, effect a great reduction in the bulk of material to be handled.

The following are the details of this part of the isolation process which the authors have applied to numerous samples of extract of West African capsicums kindly prepared for them by Messrs. James Woolley, Sons and Co., of Manchester.

The extract (450 grams) is mixed with hot water (900 c.c.) and ammonia (25 c.c.; D 0.880) previously diluted with several times its bulk of cold water. On stirring, the whole forms an apparently homogeneous solution; it is heated on the water-bath and 90 grams of finely powdered hydrated barium chloride are sifted in very slowly with constant stirring. At this stage the liquid, which contains much brown, semi-fluid deposit, and should have a strong odour of ammonia, is allowed to cool and is separated mechanically from the bulk of the insoluble deposit, filtered, and extracted with ether. The ether is further utilised to extract the deposit, although the latter is subsequently washed several times with fresh ether in order to secure the whole of the contained capsaicin. The united ethereal extracts are evaporated and provide usually about 50—80 grams of "concentrated extract" of capsaicin.

The most satisfactory method of proceeding to the isolation of capsaicin from this "concentrated extract" is to subject it at once to treatment with methyl-alcoholic barium hydroxide in order to

destroy impurities of fatty nature. For this purpose the extract is dissolved in several times its weight of methyl alcohol, the solution heated to boiling, and finely powdered barium hydroxide sifted in at intervals until the solution remains alkaline without further addition after several hours' boiling. Glacial acetic acid is now added cautiously until the solution has permanently lost all alkalinity (towards phenolphthalein), when the methyl alcohol is removed by distillation. The residue is now extracted repeatedly with dry acetone, and the latter recovered by evaporation, when the residue contains practically the whole of the capsaicin which was present in the original extract. A repetition of the last process of extraction with dry acetone is perhaps as a rule desirable, as the whole success of the application of this solvent for the removal of barium salts depends on the exclusion of moisture, which is not easy to secure in the first operation.

The residue still contains traces of impurities of both neutral and acid character. It is subjected to treatment similar to that applied by Thresh to a much more impure material (*Pharm. J.*, 1876, [iii], 7, 260), that is to say, it is dissolved in aqueous sodium hydroxide (5 per cent.), the solution extracted with ether to remove traces of neutral material and then saturated with carbon dioxide, when the precipitate is isolated by extraction with ether. The precipitate yields capsaicin in crystalline form most readily by a device also employed by Thresh and applied by the present authors as follows:

Crude capsaicin (10 grams) is dissolved in aqueous sodium hydroxide (100 c.c. of 2 per cent.) and warmed on the water-bath until the temperature is about 60°. A warm saturated solution of ammonium chloride is then gradually added until a permanent turbidity is produced. On cooling, crystalline capsaicin is deposited, and may be collected. The mother liquor is again treated with ammonium chloride solution until the deposition of capsaicin ceases.

#### *Properties of Capsaicin.*

Many of the more evident properties of capsaicin have already been described by previous workers, and in view especially of the accurate descriptions given by Micko (*loc. cit.*) and Nelson (*loc. cit.*) only a few additional notes are necessary here.

The most highly purified specimens of capsaicin melted at 64—65°. The substance appears to be optically inactive; a solution containing 1.2146 grams dissolved in benzene and made up to 20 c.c. showed no appreciable rotatory power in a 2-dcm. tube at 15°.

Analyses of several pure samples were carried out: Found: C=71.02, 70.97, and 70.88; H=8.90, 8.85, and 9.01; N=4.7.

$C_{18}H_{27}O_3N$  requires C=70.82; H=8.85; N=4.6.

$C_{18}H_{28}O_3N$  „ C=70.59; H=9.15; N=4.6.

$C_{18}H_{29}O_3N$  requires C=70.35; H=9.44; N=4.6 per cent.

For the determination of hydroxyl, 0.2437 gram was treated with magnesium methyl iodide in amyl ether, 23.2 c.c. of methane were evolved at 70° and 770 mm.; whence OH=5.3, the theoretical percentage being 5.6.

Capsaicin is sparingly soluble in concentrated hydrochloric acid, and the saturated solution deposits it in crystals on the addition of water. It is scarcely affected when boiled for several hours with 50 per cent. aqueous sodium hydroxide, but is appreciably decomposed after several hours' heating with concentrated hydrochloric acid.

*Methylcapsaicin,  $C_{17}H_{23}ON(O\cdot CH_3)_2$ .*

This compound is prepared by dissolving capsaicin and methyl sulphate in methyl alcohol and then slowly adding excess of a solution of sodium hydroxide while the whole is kept cool. After half an hour or more the bulk of the solvent is removed, the neutral methylcapsaicin separated from the residual aqueous solution by filtration or by extraction with ether, washed, and crystallised from dilute alcohol.

Found: C=71.39; H=9.16.

$C_{19}H_{29}O_3N$  requires C=71.47; H=9.09 per cent.

Methylcapsaicin dissolved readily in most of the ordinary organic media with the exception of cold light petroleum; it is insoluble in water or alkali hydroxides. It crystallises from dilute alcohol in slender, silky needles melting at 74°, and is much less pungent than capsaicin.

This derivative appears to be slowly altered by boiling with acetyl chloride and it reacts with phosphorus pentachloride below 100°, yielding an oil containing nitrogen, which is volatile in steam and has an odour suggesting that of many nitriles. The authors propose to study the products of this reaction in greater detail in the near future. Methylcapsaicin does not appear to react with phenylhydrazine, and it is recovered unaltered after prolonged boiling with alcoholic hydroxylamine acetate.

*Reduction of Capsaicin.*

Both capsaicin and its methyl ether are attacked by many comparatively mild reducing agents, but, as a rule, imperfectly. Am-

monia is always one of the products of change, but methylamine has never been detected even in traces. Numerous experiments have been made with the object of identifying the main products, but owing to the small quantities of capsaicin attacked the results were not very decisive. In one experiment, however, 10 grams of capsaicin were treated with a very large excess of metallic sodium in boiling alcohol; the dissolved sodium was precipitated from the resulting solution as carbonate with the aid of a stream of carbon dioxide and the bulk of the solvent removed by distillation through an efficient still-head. Ammonia, free from all traces of methylamine, passed over with the alcohol. From the residue in the still there was isolated without great difficulty nearly half of the capsaicin originally taken and also a small quantity of a liquid, volatile in steam, having a somewhat fragrant odour of higher fatty alcohols. The bulk of this liquid boiled at about  $216-217^{\circ}$ . As the quantity obtained did not admit of purification for analysis the fraction  $216-217^{\circ}$  was oxidised by means of dichromate and sulphuric acid mixture; the resulting fatty acid was extracted with ether, boiled with thionyl chloride, and the product shaken with concentrated aqueous ammonia. The amide of the acid was obtained in this way, and after recrystallisation from water appeared as silvery leaflets melting at  $98-100^{\circ}$ .

*Oxidation of Methylcapsaicin with Potassium Permanganate.*

Pure methylcapsaicin (10 grams) was dissolved in 3 litres of acetone and finely powdered potassium permanganate was very gradually added until a permanent pink tinge persisted in the solution—this operation occupied about two days—the temperature of the solution never being allowed to exceed  $25^{\circ}$ . The manganese dioxide was filtered off and washed repeatedly with acetone, the washings being added to the main filtrate and then evaporated.

The residue so obtained, which consisted of a viscid, reddish-brown, semi-solid oil, was subjected to steam distillation from acid solution. The distillate contained a very small quantity of a fatty acid, which was isolated in the usual manner; it was converted into its amide and gave a crystalline product, which melted at  $98-99^{\circ}$  and was apparently identical with that obtained from the oxidation of the alcohol referred to in the previous experiment, but the yield was extremely small and did not amount to more than 0.05 gram.

The residue, non-volatile in steam, was rendered alkaline with sodium carbonate and then extracted with ether. The ethereal solution yielded slightly more than 5 grams of unchanged methylcapsaicin. The sodium carbonate solution after removal of the methyl-

capsaicin gave nearly 2 grams of an acid, which readily crystallised from hot water in hard, flat needles melting at  $179-180^{\circ}$ . This acid yielded a chloride melting at  $69^{\circ}$  and an amide melting at  $163^{\circ}$ . Veratric acid, chloride, and amide melt at  $70^{\circ}$  and  $164^{\circ}$  respectively, and when mixed with the above products from methylcapsaicin were unchanged in melting point. The acid was dried in the steam-oven and analysed. (Found, C=59.4; H=5.4.  $C_9H_{10}O_4$  requires C=59.3; H=5.5 per cent.)

There is therefore no doubt that the acid was veratric acid.

#### *Oxidation of Methylcapsaicin with Chromic Acid.*

Methylcapsaicin was oxidised by a boiling solution of chromic acid in dilute sulphuric acid. The liquid was then subjected to a current of steam and oily drops passed over. The whole of the distillate was rendered alkaline with sodium carbonate and evaporated almost to dryness; it was then carefully acidified and an oily acid was liberated which was extracted with ether. The product had a strong odour of acetic acid and was therefore exposed over solid potassium hydroxide in a desiccator for several days. The odour of the acetic acid disappeared and gave place to a rather pleasant one recalling that of *n*-nonoic acid. The colourless oil ultimately obtained was cooled in ice-water, when it readily solidified to a crystalline mass which melted sharply at  $12^{\circ}$  (nonoic acid melts at  $12.5^{\circ}$ ). It also yielded an amide melting at  $98-99^{\circ}$ , which was in no respect distinguishable from the amide of *n*-nonoic acid prepared from the pelargonic acid of commerce.

The investigation is being continued.

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NOTE.—Since the work recorded in the foregoing pages was completed, the authors' attention was called to the paper by Nelson (*J. Amer. Chem. Soc.*, 1919, **61**, 1115), which renders certain of their previous views obsolete.

*Inter alia*, Nelson has obtained from capsaicin by the action of acids and alkalis under pressure vanillylamine and a decylenic acid, the latter having a branched chain. He concludes that capsaicin is a condensation product of vanillylamine and a decylenic acid.

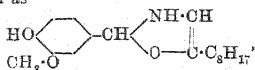
The present authors at first suspected that the fatty acid repeatedly referred to in their own communication was identical with this decylenic acid. They obtained their acid in very small



quantities, and the quantity of amide available for a combustion was only 0.0921 gram (Found, C=68.7; H=12.3.  $C_9H_{19}ON$  requires C=68.8; H=12.1 per cent.), whilst its properties as well as those of its amide closely resembled those of *n*-nonoic acid; thus when super-cooled the acid at once solidified when seeded with *n*-nonoic acid, and the amide, as already mentioned, could not be distinguished by appearance or by a mixed melting-point determination from the amide of *n*-nonoic acid.

Since the authors' attention was called to Nelson's work, the supposed nitrile obtained directly from methylcapsaicin by the action of inorganic acid chlorides has successfully been converted by means of hydrogen peroxide and dilute sodium hydroxide at 40° into an acid amide melting at 98—100°.

The present authors are not fully disposed to accept Nelson's view of the constitution of capsaicin as final. His conception of capsaicin as an acid amide is not easily reconciled with the somewhat ready reduction of a part of capsaicin to ammonia and an aliphatic alcohol boiling at about 216—217°; its distinctly basic character and the great stability of the substance towards alkalis are also somewhat difficult to understand. They originally hazarded the view that capsaicin was probably a derivative of dihydro-oxazole, and the possibility is not wholly excluded that capsaicin is built with a ring structure such as



for under the energetic conditions used by Nelson internal oxidation or molecular rearrangement would not be surprising.

### XCVIII.—*The Vapour Pressures and Densities of Mixtures of Acetone and Methyl Ethyl Ketone.*

By TUDOR WILLIAMS PRICE.

MUCH work, both theoretical and practical, has been done on the vapour pressures of binary mixtures, notably by Duhem, Lehfeldt, Ostwald, Roozeboom, Zawidski, and Young. It has been shown that for binary mixtures the components of which are miscible in all proportions, the vapour pressure at any one temperature may lie between those of the components; it may be higher or lower than that of either component.

If, however, the two components are closely related, the curvature of the graph, representing the relation between vapour pressure and concentration for any particular temperature, should not be great. According to Guthrie (*Phil. Mag.*, 1884, [v], 18, 517), if there is no heat or volume change on mixing the two components, the relation between vapour pressure and percentage composition by weight, expressed graphically, should be a straight line, but this does not generally hold.

Van der Waals (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 3, 170) considers that, if the critical pressures of the two substances are equal or nearly so, and if the molecular weight of each is normal in both the liquid and gaseous states, and if the relation suggested by Galitzine and by Berthelot holds good, that is, if  $a_{1.2} = \sqrt{a_1 \cdot a_2}$ , where  $a_{1.2}$  represents the attraction of the unlike molecules, and  $a_1$  and  $a_2$  the attraction of the like molecules, then the relation between the vapour pressure and molecular composition should be represented by a straight line, that is,

$$P = \frac{p \cdot P_A + (100 - p)P_B}{100},$$

where  $P$ ,  $P_A$ , and  $P_B$  are the vapour pressures of the mixture and the two components  $A$  and  $B$  at the same temperature, and  $p$  is the molecular percentage of liquid  $A$  in the mixture.

This relation has been verified many times, notably by Young, for mixtures such as chlorobenzene and bromobenzene, which are closely related. When the components are very closely related, but have different critical pressures, the percentage difference between the observed and calculated pressures  $\frac{100 P' - P}{P}$  for the mixtures at any temperatures is very small, even when there is molecular association in the liquid state, as with methyl and ethyl alcohol.

During the course of experiments on the production of cordite, using methyl ethyl ketone as substitute in whole or in part for acetone as the gelatinising agent, it was found that some abnormalities were obtained in the volatility of the samples. For example, a cordite gelatinised by a mixture of equal proportions by weight of acetone and methyl ethyl ketone had a lower volatility than cordite made with acetone or with methyl ethyl ketone. This showed that the cordite gelatinised with the mixed solvent dried quicker than the others, presumably owing to the fact that the 50 per cent. mixture of acetone and methyl ethyl ketone has a greater vapour pressure than either of its two components.

This supposition, although unlikely because of the close relation-

ship between acetone and methyl ethyl ketone, is not outside the bounds of possibility, owing to the great difference between their critical pressures, which are given as 52.2 and 60.0 atmospheres for acetone (Sazotschewsky, in Landolt and Bornstein's "Tabellen") and 47.5 atmospheres for methyl ethyl ketone (Grassi, *Nuovo Cim.*, 1914, [vi], 7, i, 313).

It was recognised that vapour-pressure measurements of the pure solvents and their mixtures would not furnish an absolute guide to the rate of escape of solvent from cordite on drying, because of the colloidal nature of the latter, but it was thought that such measurements would throw some light on the abnormal behaviour of cordite made with mixed solvent when being dried. Accordingly, a series of vapour pressure determinations were carried out, the results of which are given below.

#### EXPERIMENTAL.

*Materials.*—The acetone was prepared from commercial acetone as follows. After drying and fractionation, it was treated with sodium iodide according to Shipsey and Werner's method (T., 1913, 103, 1255). The white, needle-shaped crystals of the additive compound,  $\text{NaI} \cdot 3\text{C}_2\text{H}_5\text{O}$ , were quickly collected, pressed between blotting-paper, and transferred to a dry distilling flask. On gently warming, the acetone distilled over. The distillate was dried over fused calcium chloride for twenty-four hours and distilled through a five-bulb column. The fraction 56.15–56.25°/760 mm. was collected separately, dried again over fused calcium chloride for twenty-four hours, and fractionated as before. Practically all distilled constantly at 56.2°/760 mm. (corr.).

A sample gave the following results on analysis:

Acidity as $\text{CO}_2$ .....	= 0.0012 per cent.
"    " acetic acid .....	= Nil.
Alkalinity as $\text{N}/10\text{-H}_2\text{SO}_4$ c.c. ....	= Nil.
Turbidity with water .....	= Nil.
Residue on evaporation .....	= 0.0003 per cent.
Permanganate test .....	= 50 minutes.

The methyl ethyl ketone was freed from acetone by two washings with saturated brine, in which it is not very readily soluble. The purified ketone was dried over fused calcium chloride and fractionated through a five-bulb column. The fraction distilling at 78–80° was dried and fractionated again. From this second distillation, a fraction boiling at 79–80° was collected separately, dried,

and again fractionated. In this way, a final fraction was obtained boiling at  $79.5\text{--}79.6^{\circ}/759$  mm. (corr.). The boiling point of methyl ethyl ketone is given as  $79.57^{\circ}/760$  mm. (Marshall, T., 1906, 89, 1375).

A sample gave the following tests on analysis:

Aldehydes.....	= Nil.
Acidity as $\text{CO}_2$ .....	= 0.0002 per cent.
Alkalinity as $\text{N}/10\text{-H}_2\text{SO}_4$ c.c. ....	= Nil.
Permanganate test .....	= 20 minutes.

The liquids were kept in tightly stoppered bottles in a dark cupboard.

*Apparatus.*—The apparatus used was designed by Mr. Allan Morton (*private communication*).

It consisted of two similar barometer tubes connected at the bottom by a T-piece to each other and to a mercury reservoir, which could be raised or lowered at will. The top of each tube was sealed to a piece of capillary tube, longer than the barometer tube, which was bent over parallel to the barometer tube to which it was sealed. The bottom of each capillary tube was bent over again and dipped into small cups of mercury.

The barometer tubes were surrounded by a wide glass tube containing water, which was circulated and stirred by compressed air and kept at a constant temperature.

The method of procedure was as follows. Recently boiled mercury was placed in the reservoir, which was then raised until the mercury filled the barometer tubes and the capillaries and overflowed into the cups. The reservoir was then lowered and the mercury column broke at the junction of the capillaries with the barometer tubes, thus forming a vacuum in the latter. This was repeated until no air was left in the tubes and a perfect vacuum obtained.

The liquid the vapour pressure of which was to be measured was then placed above the mercury in one of the small cups. The mercury reservoir was raised until mercury overflowed into the cups. The cup with the liquid was then moved until the end of the capillary was in the liquid above the mercury. On lowering the reservoir, some of this liquid was drawn into one of the barometer tubes. By this means, the latter contained the necessary liquid and its vapour, whilst the other tube acted as a barometer.

A slight modification was found to be necessary for accurate work. As described by Morton, the capillary tubes are outside the water-jacket, and are consequently at a lower temperature than the observation tube. Liquid from the observation tube therefore

distils over and condenses above the mercury in the capillary tube, thus causing an appreciable alteration of the concentration in the case of a mixture. This difficulty was overcome by making the water-jacket wider, so as to contain the capillary tubes and to keep them at the same temperature as the observation tube.

Two thermometers were used in the work, one reading from  $0^{\circ}$  to  $50^{\circ}$  in tenths, and the other from  $50^{\circ}$  to  $100^{\circ}$  in tenths. These were carefully standardised by comparison with thermometers which had recently been tested at the National Physical Laboratory, and could easily be read to  $0.01^{\circ}$ . The temperature of the water surrounding the observation tubes was kept constant to within  $0.05^{\circ}$ , and all readings of the mercury and solvent levels were taken through a cathetometer.

A quantity of liquid remained in the observation tube above the mercury, and for this a correction had to be applied, obtained from the densities of the mixtures at the required temperature.

The densities were determined in a Regnault specific gravity bottle for liquids, of about 50 c.c. capacity, fitted with a capillary stem widening out into a cup-shaped reservoir fitted with a ground-glass stopper. All weighings were done on a balance sensitive to 0.0001 gram with standardised brass weights, and in the neighbourhood of 760 mm. pressure, and hence no correction was made for changes in atmospheric pressure. The balance case was kept dry by means of dishes containing calcium chloride, so that no correction was made for the relative humidity of the air.

A counterpoise of the same kind of glass and of the same shape as the specific gravity bottle was used in all weighings, and all weights were reduced to a vacuum.

The thermostat was provided with a thermoregulator and mechanical stirrer, and could be kept at the desired temperature within  $0.05^{\circ}$ .

For the pure liquids, determinations were made in duplicate; these agreed very closely, and the mean is given. For the mixtures, determinations were carried out in duplicate on the same solution, there being not sufficient material to make up two separate solutions of the same concentration.

*Results.*—The vapour pressures obtained are given in table I. Each figure is the mean of three or four determinations at the same temperature, which agreed very closely.

TABLE I.

*Vapour Pressures of Mixtures of Acetone and Methyl Ethyl Ketone at Various Temperatures.*

Composition of mixture.		Vapour pressure in mm. at following temperatures.						
Percentage of acetone by weight.	Molecular percentage of acetone.	20°	25°	30°	35°	40°	45°	50°
100	100	186.3	232.0	284.6	348.1	425.3	510.8	620.9
75	78.83	167.8	—	255.5	—	379.1	—	548.2
62.5	67.42	161.8	—	243.3	—	354.0	—	508.4
50	55.38	155.5	—	226.5	—	327.8	—	469.7
37.5	42.69	141.3	—	205.8	—	299.6	—	430.2
25	29.27	125.5	—	183.5	—	267.4	—	388.1
12.5	15.06	109.9	—	160.6	—	234.2	—	341.9
0	0	77.5	98.4	121.4	151.0	188.4	252.9	300.0
							(at 46.5°)	

These results are shown graphically in Figs. 1 and 2. Fig. 1 shows the relation between vapour pressure and concentration (by weight) over the whole range from pure acetone to pure methyl ethyl ketone at the temperatures indicated, whilst Fig. 2 shows the relation between vapour pressure and temperature for the pure substances and all the mixtures.

The densities are given in table II.

TABLE II.

*Densities of Mixtures of Acetone and Methyl Ethyl Ketone at Various Temperatures.*

Composition of mixture.		Density at following temperatures.			
Percentage of acetone by weight.	Molecular percentage of acetone.	20°/4°.	30°/4°.	40°/4°.	50°/4°.
100	100	0.79082	0.77931	0.76784	0.75599
75	78.83	0.79428	0.78311	0.77181	0.76020
62.5	67.42	0.79603	0.78495	0.77368	0.76233
50	55.38	0.79782	0.78677	0.77567	0.76439
37.5	42.69	0.79956	0.78869	0.77776	0.76664
25	29.27	0.80135	0.79061	0.77982	0.76877
12.5	15.06	0.80314	0.79249	0.78173	0.77084
0	0	0.80495	0.79442	0.78391	0.77315

*Discussion of Results.*—The accuracy of the results obtained in the vapour pressure measurements may be gauged by comparing them with results obtained by other workers. Table III affords a comparison of the various results given for acetone.

TABLE III.

*Showing Results obtained for the Vapour Pressure of Acetone by Various Workers.*

Vapour pressure of acetone in mm. of mercury.				
Temperature	Author.	Regnault. <sup>1</sup>	Sameshima. <sup>2</sup>	Taylor. <sup>3</sup>
20°	186.3	179.6	184.8	182.5
25	232.0	—	229.2	229.0
30	284.6	281.0	282.7	281.0
35	348.1	—	346.4	343.0
40	425.3	420.2	421.5	416.0
45	510.8	—	510.5	505.0
50	620.9	620.9	612.5	607.0

<sup>1</sup> Obtained from Landolt and Bornstein's "Tabellen."

<sup>2</sup> *J. Amer. Chem. Soc.*, 1918, **40**, 1482.

<sup>3</sup> *J. Physical Chem.*, 1900, **4**, 436.

The agreement between the present results and those of Sameshima is good, except at 50°, at which temperature better agreement is obtained with Regnault.

The results show, however, that the apparatus is capable of giving accurate results, and does away with the necessity of using stopcocks, with their attendant troubles due to leakiness and the presence of grease. The chief source of error is the possibility of the liquid absorbing air before being carried over into the observation tube. With pure liquids, this possibility can be obviated to a large extent by boiling immediately before introduction, but with mixtures this procedure would alter the concentration, and hence the above possibility must not be neglected.

As regards methyl ethyl ketone, no figures have been found in the literature for the vapour pressure at temperatures between 20° and 50°.

An examination of Fig. 1 shows that the vapour pressure-concentration curves lie between the vapour pressures of the two components at all temperatures, thus negating the suggestion that there might be a mixture of acetone and methyl ethyl ketone having a higher vapour pressure than either component. Hence the explanation of the abnormality of the volatility of cordite gelatinised with a mixture of equal parts of acetone and methyl ethyl ketone, based on the above suggestion, is unfounded.

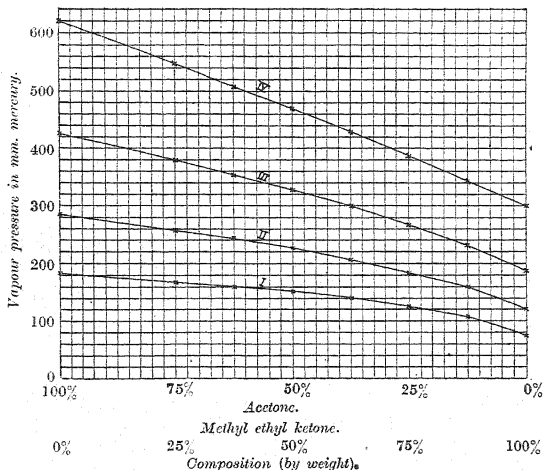
The graphs in Fig. 1 are not straight lines, but they approximate thereto, and this approximation is nearer as the temperature is increased. The deviation from a straight line, for the curve at 50°, is given in table IV by comparing the observed vapour pressures of the mixtures with those calculated according to the expression

$$P = m \cdot P_A + (100 - m) \frac{P_B}{100}$$

where  $m$  is the molecular percentage of acetone in the mixture and  $P_A$  and  $P_B$  are the vapour pressures of acetone and methyl ethyl ketone respectively.  $P'$  is the observed vapour pressure of the mixture and  $\frac{(P - P')}{P'}100$  is the percentage difference.

FIG. 1.

Showing relation between vapour pressure and composition (by weight) of mixtures of acetone and methyl ethyl ketone



Curve I. at 20°      Curve III. at 40°  
 „ II. „ 30      „ IV. „ 50

TABLE IV.

Difference between Observed and Calculated Vapour Pressures of Mixtures of Acetone and Methyl Ethyl Ketone at 50°.

Molecular percentage of acetone = $m$ .	Observed v.p. in mm. of Hg = $P'$ .	Calculated v.p. in mm. of Hg = $P$ .	$100 \frac{(P - P')}{P'}$
78.83	548.2	553.0	+0.88
67.42	508.4	516.3	+1.55
55.38	469.7	477.7	+1.70
42.69	230.2	437.0	+1.58
29.27	388.1	393.9	+1.50
15.06	341.9	348.3	+1.87

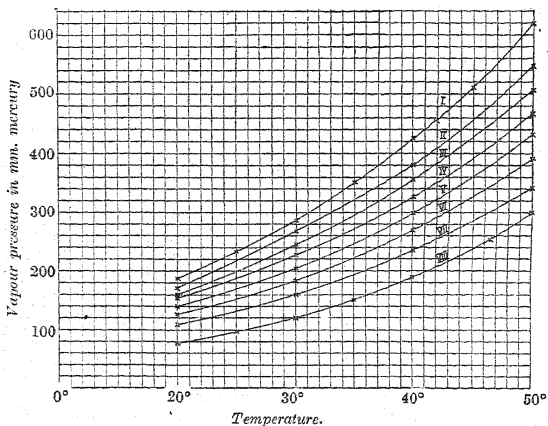


The maximum deviation is about 1.9 per cent. In Fig. 2, the curves have the familiar shape associated with vapour pressure-temperature curves, and when the logarithms of vapour pressure are plotted against temperature for each mixture and for the pure solvents, the resulting graph is practically a straight line.

There is a considerable difference in the figures given in the

FIG. 2.

*Showing relation between temperature and vapour pressure for mixtures of acetone and methyl ethyl ketone.*



Curve	I. = Acetone.	Curve	V. = 37½% Acetone (by wt.)
"	II. = 75% Acetone (by wt.)	"	VI. = 25% " " "
"	III. = 62½% " " "	"	VII. = 12½% " " "
"	IV. = 50% " " "	"	VIII. = 100% Methyl ethyl ketone.

literature for the density of acetone. Thus Perkin (T., 1884, 45, 478) gives  $D_{15}^{15}$  0.79652, which is equivalent to  $D_4^{20}$  0.79072.

Linnemann (T., quoted by Perkin) gives  $D_{15}^{15}$  0.7975 or  $D_4^{20}$  0.79170. Perkin's value is considerably lower, and was obtained with acetone purified by the sodium hydrogen sulphite method and boiling at 55.6–55.9°. McElroy and Krug (*J. Soc. Chem. Ind.*, 1893, 12, 177) give  $D_4^{20}$  0.79197. Squibb (*J. Amer. Chem. Soc.*, 1895, 17, 200) gives  $D_{15}^{15}$  0.7966 or  $D_4^{20}$  0.7908. This value agrees closely with that obtained by Perkin. Bramley (T., 1916, 109, 455) obtained

the value  $D_4^{20}$  0.7912. Thus the range of published figures varies from 0.79072 to 0.79197 for the density of acetone at  $20^\circ/4^\circ$ . The result obtained in the present work is the mean of two which agreed exactly, namely, 0.79082. The specific gravities in this work are given to five decimal places, by which is meant that they are correct to four places, the fifth figure being doubtful in each case. It will be seen, therefore, that excellent agreement is obtained with the result of Squibb ( $D_4^{20}$  0.7908) and with that of Perkin ( $D_4^{20}$  0.79072).

The results for the density of acetone at other temperatures agree well with those obtained by Bramley (*loc. cit.*), as shown in the following table.

TABLE V.

*Comparison of Results for Density of Acetone at Various Temperatures.*

Temperature.	Density.	
	Author.	Bramley.
$20^\circ/4^\circ$	0.79082	0.7912
$30^\circ/4^\circ$	0.77931	0.7793
$40^\circ/4^\circ$	0.76784	0.7674
$50^\circ/4^\circ$	0.75599	0.7555

The density of methyl ethyl ketone is given by Marshall (T., 1906, 89, 1376) as 0.81005 at  $15^\circ/4^\circ$ . Extrapolation from the results obtained by the present author gives 0.8101, which agrees very well with Marshall's figure.

The density-concentration curves are all straight lines parallel to each other, thus showing that there is no contraction or expansion in volume on mixing acetone and methyl ethyl ketone at any of the temperatures  $20^\circ$  to  $50^\circ$ .

The density-temperature curves for the pure liquids and for the mixtures are also practically straight lines, the curvature being extremely slight. For acetone, the difference in density per degree over the whole range is 0.001161, and for methyl ethyl ketone it is 0.00106.

#### *Summary.*

Vapour pressures and densities of acetone, methyl ethyl ketone, and mixtures of the two have been determined from  $20^\circ$  to  $50^\circ$ .

The vapour pressure-concentration curves all lie between the vapour pressures of the components, there being no sign of a maximum at any point.

The density-concentration curves are straight lines, showing that

no change in volume occurs when acetone and methyl ethyl ketone are mixed in any proportions from 20° to 50°.

In conclusion, the author's best thanks are due to Messrs. Nobel's Explosives Co., Ltd., for whom the work was carried out, and to Mr. Wm. Rintoul, the Manager of the Research Section, for permission to publish the results.

THE RESEARCH LABORATORIES,  
ARDEER.

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## XCIX.—*The Constitution of Internal Diazo-oxides (Diazophenols). Part II.*

By GILBERT T. MORGAN and ERIC DODDRELL EVENS.

EARLIER experiments on the nitrated ortho- and para-diazo-oxides of the benzene series showed that 4-nitrobenzene-1-diazo-2-oxide obtained by the diazotisation of 5-nitro-2-aminophenol has the property of forming dihydroxyazo-derivatives which yield metallic lakes having remarkably distinctive colours (Morgan and Porter, T., 1915, 107, 645).

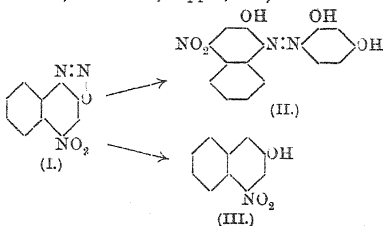
In the present investigation the corresponding diazo-oxide of naphthalene has been examined from this point of view. The results afford an interesting comparison of the differences manifested between benzenoid diazo-oxides and their analogues in the naphthalene series.

4-Nitronaphthalene-1-diazo-2-oxide (I) was first obtained by Friedländer, who passed nitrous fumes into a solution of 2:4-dinitro- $\alpha$ -naphthylamine in moderately concentrated sulphuric acid and added the diazo-solution to alcohol or water (*Ber.*, 1895, 28, 1951).

The product, which can be prepared in quantitative yield by the methods described in the present paper, has not hitherto been examined in any detail. This very stable internal diazo-oxide couples only with the more reactive phenols, such as resorcinol, phloroglucinol, and 1:3-dihydroxynaphthalene, and in these instances the formation of azo-compounds takes place not only in alkaline solutions but also, and with greater facility, in the presence of strong acids, for example, in glacial acetic acid containing concentrated mineral acid.

4-Nitro- $\beta$ -naphthol-1-azoresorcinol (II) functions as an acid mordant dye giving reddish-brown shades on wool which are changed

into lakes of characteristic colour by the action of metallic mordants (chromium, vanadium, copper, etc.):



On prolonged boiling with ethyl alcohol either alone or in the presence of a metallic catalyst, 4-nitronaphthalene-1-diazo-2-oxide loses its diazo-group and becomes converted into 4-nitro-β-naphthol (III), the fourth isomeride to be discovered of the seven possible nitro-β-naphthols.

4-Nitro-β-naphthol is less reactive than β-naphthol. It is much less easily alkylated, and couples more slowly with azo-compounds. The 4-nitro-1-azo-β-naphthols, from benzenediazonium chloride and *p*-nitrobenzenediazonium chloride, are insoluble in aqueous alkali hydroxides, in this respect resembling the azo-β-naphthols, the insolubility of which in aqueous alkalis is a matter of so much theoretical interest and industrial importance. The azo-dyes obtained from 4-nitro-β-naphthol differ considerably in colour from those derived from β-naphthol.

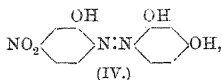
The diazotisation of 2:4-dinitroaniline in concentrated sulphuric acid has already been effected, and the results indicate that the nitro-group is less readily removed than in the foregoing case of 2:4-dinitronaphthalene-1-diazonium sulphate. The elimination of a nitro-group from 2:4-dinitrobenzene-1-diazonium sulphate is not effected merely by dilution with water. In this instance it is necessary to neutralise the solution with alkali carbonate (Badische Anilin- & Soda-Fabrik, D.R.-P., 144640), when a soluble form of 5-nitro-2-diazophenol is produced. Repetition of this experiment showed that the formation of this ortho-diazophenol is not quantitative. An insoluble product is obtained, the amount of which varies from 14 to 20 per cent. of the 2:4-dinitroaniline employed. This by-product, which is still under examination, is an ill-defined substance having the properties of an external diazo-oxide. It couples readily with either alkaline β-naphthol or β-naphthylamine in acetic acid solution.

The soluble variety of 5-nitro-2-diazophenol contained in the

clear, yellow filtrate from the foregoing insoluble product couples with aromatic *m*-diamines, phenols, naphthols, aminonaphthols, and their sulphonic acids.

The azo- $\beta$ -naphthol thus obtained is identical with the compound produced from the insoluble 4-nitrobenzene-1-diazo-2-oxide (M. and P., T., *loc. cit.*).

5-Nitrophenol-2-azoresorcinol (IV),



gives intensely coloured lakes on wool mordanted with metallic hydroxides. Similar dihydroxyazo-dyes are obtained from chromotropic acid and from aminonaphtholsulphonic acids coupled in alkaline solution. These colouring matters are extremely sensitive to metals, and are converted into green, purple, and blue lakes by the action of metallic mordants.

#### Summary.

1. 2:4-Dinitronaphthalene-1-diazonium sulphate is unstable in dilute acid and passes quantitatively into the sparingly soluble 4-nitronaphthalene-1-diazo-2-oxide, a very stable diazo-oxide yielding azo-derivatives only with difficulty.

2. 4-Nitronaphthalene-1-diazo-2-oxide undergoes loss of the diazo-group with the production of 4-nitro- $\beta$ -naphthol.

3. 2:4-Dinitrobenzene-1-diazonium sulphate is stable in dilute acid, but in neutral or slightly alkaline solution it yields the soluble 5-nitro-2-diazophenol together with an insoluble by-product. This soluble diazo-compound furnishes *o*-dihydroxyazo- and *o*-amino-hydroxyazo-dyes, giving intensely coloured lakes with metallic mordants.

#### EXPERIMENTAL.

##### *I. Diazotisation of 2:4-Dinitro- $\alpha$ -naphthylamine Sulphate.*

2:4-Dinitro- $\alpha$ -naphthylamine, the starting point of this part of the investigation, was obtained in three different ways.

1. *Preparation from 2:4-Dinitro- $\alpha$ -naphthol.*—Finely powdered  $\alpha$ -naphthol (50 grams) was added to 100 c.c. of concentrated sulphuric acid and the mixture stirred until a clear solution was obtained. On heating this liquid on the water-bath for fifteen minutes,  $\alpha$ -naphtholdisulphonic acid separated when the mixture

was cooled, and the solidified mass was dissolved in 250 c.c. of water. The cooled solution was added slowly to 60 c.c. of nitric acid (D 1.42), the temperature being maintained below 10°. The nitration mixture was then slowly warmed to 100° and maintained at this temperature for fifteen minutes, the pasty mass being stirred continuously. After cooling, the pale yellow 2:4-dinitro- $\alpha$ -naphthol was collected (m. p. 132°; yield, 83 per cent.).

The authors are indebted to Dr. L. G. Paul for this process, in which the nitration is much more under control than when the nitric acid is added to solutions of  $\alpha$ -naphtholdisulphonic acid. Prolonged sulphonation on the water-bath led to  $\alpha$ -naphtholtrisulphonic acid with subsequent formation of naphthol yellow S.

Dinitro- $\alpha$ -naphthol (60 grams) and 700 c.c. of alcoholic ammonia saturated at 0° were heated for ten hours at 195–200° in a rotating steel autoclave, the pressure attained being 39 kilos. per square cm. 2:4-Dinitro- $\alpha$ -naphthylamine (40 grams) separated from the alcoholic solution on cooling; the filtrate contained the ammonium salt of 2:4-dinitro- $\alpha$ -naphthol together with tarry impurities. When crystallised from glacial acetic acid, 2:4-dinitro- $\alpha$ -naphthylamine melted at 239°. Concentrated aqueous ammonia, under the foregoing conditions, did not affect dinitro- $\alpha$ -naphthol.

2. *Preparation from Aceto- $\alpha$ -naphthalide* (compare Meldola, *Ber.*, 1886, 19, 2683).—Aceto- $\alpha$ -naphthalide (100 grams) was dissolved in 200 c.c. of glacial acetic acid and nitrated with 52 c.c. of nitric acid (D 1.52) mixed with an equal volume of glacial acetic acid. During the addition of the mixed acids, the temperature was kept below 70° and subsequently raised to 96° until the dinitro-compound began to separate. The mixture was then cooled and the separating solid crystallised from glacial acetic acid (yield, 52 per cent.). Twenty grams of purified 2:4-dinitroaceto- $\alpha$ -naphthalide were added to a cold mixture of 30 c.c. of water and 200 c.c. of concentrated sulphuric acid. The mixture was warmed at 60–70° for a few minutes, allowed to cool for fifteen minutes, and poured into 400 c.c. of ice-water, when 2:4-dinitro- $\alpha$ -naphthylamine was precipitated.

3. *Preparation from Toluene-*p*-sulphon- $\alpha$ -naphthylamide*.—Toluene-*p*-sulphon- $\alpha$ -naphthylamide, prepared by triturating together  $\alpha$ -naphthylamine, toluene-*p*-sulphonyl chloride, and anhydrous sodium acetate in molecular proportions, was washed with warm water rendered alkaline with sodium carbonate and crystallised from alcohol (yield, 96 per cent.). Fifty grams of this preparation were dissolved in 400 c.c. of hot glacial acetic acid. The solution when cooled to 45° deposited crystals of the dissolved substance, and the mixture was nitrated with 30 c.c. of nitric acid

(D 1.42) mixed with 30 c.c. of glacial acetic acid. The temperature rose to 60° and the mixture was subsequently heated to 80° for one hour. On cooling, *toluene-p-sulphon-2:4-dinitro- $\alpha$ -naphthylamide* crystallised, and a further crop was obtained on diluting with water. When crystallised from alcohol this compound separated in radiating clusters of pale yellow, silky needles melting at 165—166° (yield, 80 per cent.):

0.3614 gave 36.3 c.c.  $N_2$  at 22° and 763.6 mm.  $N = 11.42$ .

$C_{17}H_{13}O_6N_3S$  requires  $N = 10.85$  per cent.

This dinitro-compound was hydrolysed by adding 20 grams to a cooled mixture of 200 c.c. of concentrated sulphuric acid and 30 c.c. of water, and warming at 70° for ten minutes. On adding the cooled mixture to ice-cold water, 2:4-dinitro- $\alpha$ -naphthylamine was precipitated, the yield being quantitative.

#### 4-Nitronaphthalene-1-diazo-2-oxide (I).

2:4-Dinitro- $\alpha$ -naphthylamine (3 grams) was dissolved in 30 c.c. of cold concentrated sulphuric acid, 5.5 grams of nitrosyl sulphate were added, and the solution was diluted with fragments of ice until on further dilution of a portion with water a clear solution was obtained. The main solution of diazotised amine was then poured into 800 c.c. of water and left for one hour, when the precipitated diazo-oxide was collected and crystallised from light petroleum (b. p. 60—80°). This product, which separated in yellow needles, decomposed with intumescence at 130—134°.

The foregoing diazotisation was also effected with dry sodium nitrite dissolved in concentrated sulphuric acid at temperatures below 70°, the solution being cooled before use. Moreover, the diazo-oxide was prepared from the acyl derivatives of 2:4-dinitro- $\alpha$ -naphthylamine without isolating the base itself.

2:4-Dinitroaceto- $\alpha$ -naphthalide (30 grams) or the corresponding amount of *toluene-p-sulphon-2:4-dinitro- $\alpha$ -naphthylamide* added to 300 c.c. of concentrated sulphuric acid diluted with 42 c.c. of water underwent hydrolysis on warming to 70°. After cooling to 0° the solution was treated with 10 grams of sodium nitrite dissolved in 30 c.c. of concentrated sulphuric acid. Fragments of ice were added until a test portion on further dilution with water gave no precipitate of undiazotised amine. The solution was then poured into 1 litre of ice-water. A clear solution was produced, which after thirty seconds became cloudy and deposited a crystalline, brownish-yellow precipitate of the diazo-oxide (yield, 92 per cent.).

4-Nitronaphthalene-1-diazo-2-oxide was very sparingly soluble in water; it dissolved readily in benzene, acetone, or acetic acid, and

crystallised from these solvents. It was moderately soluble in alcohol, and on adding sodium hydroxide to this solution nitrogen was evolved and acetaldehyde produced.

With resorcinol, phloroglucinol, or 1:3-dihydroxynaphthalene the diazo-oxide reacted in alcoholic solution on the addition of a drop of aqueous sodium hydroxide, giving a blue coloration which can be used as a test for this diazo-derivative.

4-Nitronaphthalene-1-diazo-2-oxide has the remarkable property of coupling to form azo-compounds with the foregoing polyhydric phenols in a mixture of concentrated hydrochloric and acetic acids. It is, however, only with these very reactive phenols that this diazo-oxide has been found to combine.

#### *4-Nitro-β-naphthol-1-azoresorcinol (II).*

Five grams of 4-nitronaphthalene-1-diazo-2-oxide and 2.5 grams of resorcinol were dissolved in 50 c.c. of glacial acetic acid to which 5 c.c. of concentrated hydrochloric acid were added. After two days about 1 gram of the hydroxyazo-compound had separated, and on concentrating the filtrate a further 0.5 gram was obtained.

On pouring the filtrate into water, 5 grams of somewhat tarry azo-compound separated. The crystalline portions were crystallised repeatedly from glacial acetic acid, when the compound separated in reddish-black, nodular crystals melting at 254—256°:

0.1942 gave 20.25 c.c.  $N_2$  at 18° and 762 mm.  $N=12.13$ .

$C_{16}H_{11}O_5N_3$  requires  $N=12.92$  per cent.

4-Nitro-β-naphthol-1-azoresorcinol gave indigo-blue alkali salts in aqueous alkali hydroxides and developed an intense violet coloration with concentrated sulphuric acid. Although only sparingly soluble in water, this hydroxyazo-compound can be employed as an acid mordant dye. On unmordanted wool it furnished reddish-brown shades, becoming violet on subsequent treatment with copper sulphate and acetic acid. On chromium mordanted wool a bluish-black lake was produced. 4-Nitronaphthalene-1-diazo-2-oxide when coupled with phloroglucinol or 1:3-dihydroxynaphthalene in the presence of glacial acetic acid and concentrated hydrochloric acid gave rise to similar hydroxyazo-compounds dyeing chrome-mordanted wool in bluish-violet shades. Like the preceding substance these hydroxyazo-derivatives dissolved readily in the ordinary organic solvents, but showed very little tendency to crystallise. They gave rise to blue alkali salts and developed violet colorations with concentrated sulphuric acid.



*4-Nitro-β-naphthol* (III).

4-Nitronaphthalene-1-diazo-2-oxide (40 grams) was heated in a reflux apparatus with 600 c.c. of alcohol and 12 grams of finely divided copper for twelve hours. Acetaldehyde was evolved, and at the end of this period a drop of the solution tested with alkaline resorcinol no longer gave a blue coloration. This negative result indicated the absence of unaltered diazo-oxide, whereas the production of a red azo-dye with diazotised sulphanilic acid revealed the presence of a phenolic compound.

The filtered solution was evaporated to remove alcohol, and the residue extracted repeatedly with hot water. On cooling, the aqueous extracts furnished yellow, felted needles of 4-nitro-β-naphthol (yield about 38 per cent. of the theoretical). The copper precipitate contained an intensely coloured organic compound insoluble in alcohol, but dissolving in pyridine or aniline to a deep blue solution and in nitrobenzene to a purple solution. This product, owing to its insoluble, uncrystallisable nature, was not examined further.

Many experiments were carried out on the preparation of 4-nitro-β-naphthol, and it was found that other metals gave better results than copper in the reduction of the diazo-oxide.

With zinc dust (8 grams) and the foregoing proportions of diazo-oxide and alcohol the reduction was complete after boiling for sixteen hours, the yield of recrystallised 4-nitro-β-naphthol being 45 per cent. of the theoretical. The optimum result was obtained with powdered aluminium (7 grams) added to 70 grams of the diazo-oxide suspended in 1050 c.c. of alcohol. This mixture when heated under reflux for thirty-two hours gave a negative test with alkaline resorcinol, and after distilling off the alcohol and acetaldehyde and extracting the residue with hot water a yield of 58—64 per cent. of 4-nitro-β-naphthol was obtained.

This decomposition was effected in twenty-six hours by heating at 50° the diazo-oxide (64 grams) suspended in alcohol (1000 c.c.) with 24 c.c. of 30 per cent. hypophosphorous acid, the yield of 4-nitro-β-naphthol being 53 per cent.

In ethyl alcohol alone without metallic catalysts a yield of 45 per cent. of 4-nitro-β-naphthol was obtained after twenty-four hours' boiling. The replacement of ethyl by butyl alcohol lowered the yield considerably, as also did the employment of formic acid and copper powder.

After repeated crystallisation from carbon tetrachloride or benzene, 4-nitro-β-naphthol melted at 120°:

0.1810 gave 12 c.c.  $N_2$  at  $25^\circ$  and 768 mm.  $N=7.48$ .

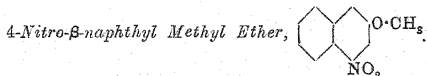
$C_{10}H_7O_3N$  requires  $N=7.41$  per cent.

4-Nitro- $\beta$ -naphthol crystallised from light petroleum (b. p.  $80-100^\circ$ ), hot water, or carbon tetrachloride in slender, yellow needles, and from benzene in compact, tabular prisms. It dissolved in aqueous alkali hydroxides to deep red solutions. Its potassium salt crystallised in glistening, red needles, but was hydrolysed on continued washing with water.

When reduced with tin and hydrochloric acid or with zinc dust and ammonium chloride in 50 per cent. alcohol, 4-nitro- $\beta$ -naphthol was reduced to 4-amino- $\beta$ -naphthol, but prolonged digestion on the water-bath with these reducing agents led to the elimination of the amino-group and the formation of 1:3-dihydroxynaphthalene (compare Friedländer, *Ber.*, 1895, **28**, 1952).

Attempts to convert 4-nitro- $\beta$ -naphthol into 4-nitro- $\beta$ -naphthylamine by heating under pressure with aqueous or alcoholic ammonia were not successful. It was not found possible to obtain a nitro-derivative of Meldola's blue by condensing 4-nitro- $\beta$ -naphthol with *p*-nitrosodimethylaniline hydrochloride in alcohol or acetic acid.

Experiments on alkylation showed that 4-nitro- $\beta$ -naphthol was much less reactive than  $\beta$ -naphthol. Boiling for twelve hours with alcohol containing 2 per cent. of sulphuric acid did not lead to ethylation of the nitro-compound.



The sodium salt of 4-nitro- $\beta$ -naphthol was suspended in dry xylene (10 parts) and boiled for eight hours with a slight excess of methyl sulphate. The solvent was evaporated, and the residue crystallised repeatedly from a mixture of benzene and alcohol:

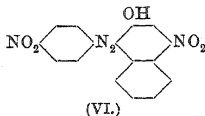
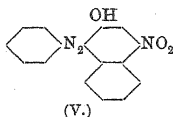
0.2227 gave 13.8 c.c.  $N_2$  at  $24^\circ$  and 760 mm.  $N=6.92$ .

$C_{11}H_9O_3N$  requires  $N=6.90$  per cent.

4-Nitro- $\beta$ -naphthyl methyl ether crystallised from a mixture of benzene and alcohol in lustrous, brown needles melting at  $100-103^\circ$ .

#### *Azo-derivatives of 4-Nitro- $\beta$ -naphthol.*

4-Nitro- $\beta$ -naphthol when dissolved in aqueous alkali hydroxides or carbonates coupled readily with various diazonium compounds.

*Benzene-1-azo-4-nitro-β-naphthol* (V),

A solution of benzenediazonium chloride added to 4-nitro-β-naphthol (1 mol.) dissolved in *N*/2-sodium hydroxide gave at once an insoluble, dark red azo-compound which, after crystallisation from benzene, separated in dark brownish-red needles melting at 206–207°:

0.2088 gave 27.6 N<sub>2</sub> at 22° and 761.5 mm. N=14.98.

C<sub>16</sub>H<sub>11</sub>O<sub>3</sub>N<sub>3</sub> requires N=14.33 per cent.

Benzene-1-azo-4-nitro-β-naphthol dissolved only sparingly in alcohol; it was insoluble in aqueous sodium hydroxide, in this respect resembling benzeneazo-β-naphthol. The nitro-group had not rendered the compound acidic. Concentrated sulphuric acid developed a magenta coloration, whilst alcoholic sodium hydroxide gave a deep red solution.

*p*-Nitrobenzene-1-azo-4-nitro-β-naphthol (VI).

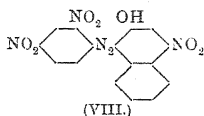
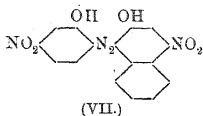
A dilute solution of *p*-nitrobenzenediazonium chloride added to 4-nitro-β-naphthol dissolved in excess of *N*/2-sodium hydroxide gave a purplish-red precipitate of the azo-derivative difficult to crystallise on account of its sparing solubility in the ordinary solvents. From glacial acetic acid the azo-compound separated in nodular crystals melting at 231°:

0.1691 gave 23.5 c.c. N<sub>2</sub> at 17° and 767.4 mm. N=16.29.

C<sub>16</sub>H<sub>10</sub>O<sub>5</sub>N<sub>4</sub> requires N=16.57 per cent.

*p*-Nitrobenzene-1-azo-4-nitro-β-naphthol, which was insoluble in aqueous alkali hydroxides, dissolved in alcoholic sodium hydroxide to an intense purplish-blue solution probably containing a quinonoid sodium salt, hydrolysed by water with the regeneration of the original azo-compound. Concentrated sulphuric acid and this azo-compound developed a purple coloration.

When developed on calico padded with alkaline 4-nitro-β-naphthol and Turkey red oil this azo-compound gave a crimson-red colour quite distinct from paranitroaniline-red. In this case deeper and more even shades were obtained when the 4-nitro-β-naphthol was dissolved in aqueous sodium carbonate rather than in sodium hydroxide solution.

*Azo-4-nitro-β-naphthols from 2:4-Dinitroaniline,*

2:4-Dinitroaniline (3 grams) dissolved in cold concentrated sulphuric acid was diazotised as described on p. 1136, and the dilute acid solution of 2:4-dinitrobenzenediazonium sulphate added to a cold solution of 4-nitro-β-naphthol (1 mol.) dissolved in excess of normal sodium hydroxide. A dark reddish-brown precipitate *A* (3 grams) was at once produced, and the filtrate from this substance gave on acidification a paler red precipitate *B* (2 grams).

The former precipitate, *A*, which was probably a sodium salt, was boiled with glacial acetic acid to set free the azo-compound, which was then crystallised from anisole. The product separated in dark brownish-red, nodular crystals melting very indefinitely at 132—166°:

0.0738 gave 10.35 c.c.  $N_2$  at 26° and 764 mm.  $N = 15.64$ .

$C_{11}H_{10}O_6N_4$  requires  $N = 15.82$  per cent.

This analytical result corresponds with formula VII for a dihydroxyazo-compound which was probably precipitated in the form of its sparingly soluble sodium salt.

The second precipitate *B* also crystallised from anisole in dark red, tabular crystals with a green reflex. This product, when boiled with alcohol to remove the solvent, melted indefinitely between 200° and 250°:

0.2020 gave 31.7 c.c.  $N_2$  at 19° and 762.4 mm.  $N = 18.09$ .

$C_{16}H_9O_7N_3$  requires  $N = 18.28$  per cent.

This result corresponds with formula VIII for an azo-compound containing three nitro-groups. This azo-4-nitro-β-naphthol containing three nitro-groups is apparently acidic and remained dissolved until the alkaline solution was acidified. The two products of this azo-coupling were not very crystallisable, but the analytical data showed that the separation by means of alkali was practically complete.

With concentrated sulphuric acid, compound *A* (VII) gave a purple coloration, whereas compound *B* (VIII) developed an indigo-blue coloration.

*Azo-colouring Matters from 4-Nitro- $\beta$ -naphthol.*

The 4-nitro-derivative of orange II was prepared by adding diazotised sulphanilic acid to 4-nitro- $\beta$ -naphthol dissolved in excess of cold  $N/2$ -sodium hydroxide. On adding sodium chloride to the solution heated on the water-bath, the dye precipitated as a dark red powder, dyeing wool in deep red shades quite unlike those obtained from orange II.

*p*-Nitroaniline-*o*-sulphonic acid diazotised and coupled with alkaline 4-nitro- $\beta$ -naphthol gave an acid azo-dye furnishing orange shades on wool.

Picramic acid diazotised and coupled with 4-nitro- $\beta$ -naphthol furnished a dye melting above  $250^{\circ}$  and giving reddish-brown shades on unchromed wool, the chrome lake being brownish-purple. The three foregoing dyes gave deep red colorations with concentrated sulphuric acid.

Calico padded with 4-nitro- $\beta$ -naphthol, aqueous sodium carbonate, and Turkey-red oil was passed through a solution of sodium acetate and the bisdiazonium chloride from dianisidine. The fabric was dyed in dark blue shades.

Primuline dyed and diazotised on cotton gave with alkaline 4-nitro- $\beta$ -naphthol a purple maroon colour, quite unlike the red ingrain dye from  $\beta$ -naphthol.

Direct cotton colours dyeing in purple shades were obtained by coupling alkaline 4-nitro- $\beta$ -naphthol with the diazo-derivatives of safranine and 4:4'-diaminostilbene-2:2'-disulphonic acid.

*II. Diazotisation of 2:4-Dinitroaniline Sulphate.*

The 2:4-dinitroaniline employed in these experiments was obtained in practically quantitative yield by heating 4-chloro-1:3-dinitrobenzene with nine parts by weight of concentrated aqueous ammonia at  $110^{\circ}$  for two hours in the rotating autoclave.

In the following experiments, 2:4-dinitroaniline was diazotised in concentrated sulphuric acid. Dry sodium nitrite (2.2 grams) was added to 7.5 c.c. of cold concentrated sulphuric acid, and the mixture heated to  $75^{\circ}$ . The clear liquid thus obtained was cooled in ice, and 5 grams of 2:4-dinitroaniline were added with stirring. After two hours, the pasty mass was diluted to 700 c.c. with ice and water. The solution at this stage contained 2:4-dinitrobenzenediazonium sulphate, as was proved by adding the liquid slowly to alkaline  $\beta$ -naphthol, when 2:4-dinitrobenzeneazo- $\beta$ -naphthol was deposited as a bright orange-red precipitate very sparingly soluble in the ordinary organic media. This product

crystallised from hot glacial acetic acid in orange-red needles, and did not melt below 270°. With cold concentrated sulphuric acid it developed a purple-blue coloration, and with alcoholic sodium hydroxide a deep blue solution.

*5-Nitro-2-diazophenol.*

Elimination of the ortho-nitro-group in 2:4-dinitrobenzene-diazonium sulphate was effected by pouring the diazo-solution, prepared as in the foregoing diazotisation, into a litre of water containing 17.4 grams of sodium carbonate and 400 grams of ice. After one hour, a yellow precipitate was collected which, on drying at the ordinary temperature, weighed 0.7 gram. The insoluble product, which melted and decomposed between 64° and 80°, coupled with alkaline  $\beta$ -naphthol, yielding a purplish-brown azo-compound. When half the amount of water was used in the neutralisation, the amount of this by-product increased to 0.9 gram.

The yellow, alkaline solution from this by-product was added to excess of alkaline  $\beta$ -naphthol, when the yellow colour of the 5-nitrodiazophenol disappeared, and a deep blue precipitate with bronze reflex was produced, the supernatant liquid having a brown tint. This blue compound was a sparingly soluble sodium salt which, on treatment with alcoholic hydrogen chloride, yielded a purplish-red azo- $\beta$ -naphthol melting at 228°, and identical with the 4-nitro-2-hydroxybenzeneazo- $\beta$ -naphthol obtained from the internal diazo-oxide of 5-nitro-2-aminophenol (T., 1915, 107, 655). The identity of the two compounds was confirmed by a mixed melting-point determination and by the formation of the characteristic metallic lakes from the foregoing preparation.

The production of a dihydroxyazo-compound from  $\beta$ -naphthol and the alkaline solution of the diazo-derivative of 2:4-dinitroaniline showed that in alkaline solution the ortho-nitro-group had been replaced by hydroxyl. This conclusion was confirmed by the following experiments.

*5-Nitrophenol-2-resorcinol (IV).*

Sodium nitrite (1.1 grams) was added to 3.75 c.c. of concentrated sulphuric acid, the temperature being kept below 70°. The warm solution was cooled, and 2.5 grams of 2:4-dinitroaniline were added. After one hour, the brown paste was added to a solution of 8.8 grams of sodium carbonate in 300 c.c. of water containing 100 grams of ice.

The yellow solution filtered from the insoluble by-product (0.4

gram) was treated with 1.5 grams of resorcinol in 5.7 c.c. of 20 per cent. aqueous sodium hydroxide. The intense purplish-red alkaline solution was subsequently warmed on the water-bath, and the sodium salt of the azo-dye precipitated by the addition of 100 grams of sodium chloride. This sodium salt (4.5 grams) gave the orange-red azo-resorcinol on treatment with dilute sulphuric acid. When crystallised from glacial acetic acid, it separated in small, reddish-brown needles decomposing at  $225^{\circ}$ . The sulphuric acid coloration was deep red:

0.0997 gave 13.75 c.c.  $N_2$  at  $21.5^{\circ}$  and 762 mm.  $N=15.67$ .

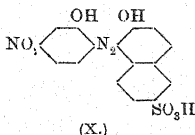
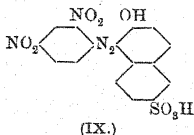
$C_{12}H_9O_5N_3$  requires  $N=15.27$  per cent.

The percentage of nitrogen required for dinitrobenzeneazo-resorcinol is 18.42.

On unchromed wool, this azo-resorcinol gave bright orange-red shades, changing to deep claret on chroming subsequently with 1 per cent. of chromic acid. By the metachrome process of dyeing, very deep purple shades were produced, appearing almost black.

The marked alteration of shade produced by mordanting with chromium suggested the arrangement of two hydroxyl groups contiguous to the azo-group, as indicated in the above formula. Further evidence was obtained by a comparative experiment made on  $\beta$ -naphthol-6-sulphonic acid.

*Azo-dyes from 2:4-Dinitroaniline and Schäffer's Acid.*



(1) 2:4-Dinitroaniline (2.5 grams) was added to a solution of 1.1 grams of sodium nitrite in 7.5 c.c. of concentrated sulphuric acid, and the resulting paste added to 150 c.c. of cold water. This acid solution of 2:4-dinitrobenzenediazonium sulphate was added to 3.5 grams of Schäffer's salt dissolved in 100 c.c. of water and 70 c.c. of 5*N*-sodium hydroxide. After one hour, the solution was heated on the water-bath and the azo-dye precipitated with 50 grams of salt. This dye, 2:4-dinitrobenzeneazo- $\beta$ -naphthol-6-sulphonic acid (IX), gave orange shades on unmordanted wool not altered by chroming.

(2) 2:4-Dinitroaniline (2.5 grams) was diazotised as before in concentrated sulphuric acid; the diluted diazo-solution was

rendered alkaline with excess of aqueous sodium carbonate and added to an alkaline solution of Schäffer's salt. After one hour, the solution was warmed and the dye precipitated with sodium chloride. This dye, 4-nitro-2-hydroxybenzeneazo- $\beta$ -naphthol-6-sulphonic acid (X), gave reddish-brown shades on wool, changing to deep violet on chroming.

(3) The dinitroaniline (2.5 grams) was diazotised as before, and to the dilute acid solution was added 3.4 grams of copper sulphate; the liquid was then rendered alkaline with sodium carbonate and added to an alkaline solution of Schäffer's salt. Coupling occurred slowly, and was completed by warming, the dye being then salted out. It gave purple shades on wool, which were not affected by after-chroming. These purple shades were reproduced by treating the dyed patterns of the second preparation with copper sulphate. Similar purple shades were obtained by treating the dihydroxyazo-dye (X) with cobalt chloride or chlorocobaltipentammine chloride,  $[\text{ClCo}(\text{NH}_3)_5]\text{Cl}_2$ .

These experiments point conclusively to the formation of a soluble form of 5-nitro-2-diazophenol when an acid solution of 2:4-dinitrobenzenediazonium sulphate is rendered alkaline with sodium carbonate.

The azo-dyes produced by coupling this alkaline diazo-solution with various phenolic derivatives and reactive amines all have the property of forming distinctly coloured metallic lakes. With 2:4-tolylenediamine, the aminohydroxyazo-dye was produced in dilute acetic acid. In the case of the aminonaphtholsulphonic acids, the coupling was effected in the presence of sodium hydroxide. With chromotropic acid, the most favourable result was obtained on using milk of lime as the alkali.

*Azo-dyes from 5-Nitro-2-diazophenol.*

Coupling substance.	Colour of dye on unmordanted wool.	Colour of mordanted dye.
2 : 4-Tolylenediamine.	—	{ Metachrome process : purplish-black lake (1 per cent.).
2-Hydroxy-3-naphthoic acid.	Reddish-brown.	Purple chromium lake.
1 : 8 - Dihydroxynaphthalene-3 : 6-disulphonic acid (chromotropic acid).	Bluish-red.	{ Chromium—greenish-blue. Vanadium—blue. Copper—bluish-purple. Cobalt—purplish-blue.
8 - Amino - $\alpha$ - naphthol - 3 : 6-disulphonic acid (H. acid).	Purple.	{ Chromium—dark green. Vanadium—green. Copper—intense blue. Cobalt—dark bluish-purple.



*Azo-dyes from 5-Nitro-2-diazophenol (continued).*

Coupling substance.	Colour of dye on unmordanted wool.	Colour of mordanted dye.
8 - Amino - $\alpha$ - naphthol - 5-sulphonic acid (S acid). }	Mauve.	Chromium—sage-green. Vanadium—bright green. Copper—bright blue. Cobalt—blue. Nickel—blue. Iron—dull violet. Manganese—dull violet. Uranium—dark lavender blue.
7 - Amino - $\alpha$ - naphthol - 3-sulphonic acid (J acid). }	Crimson-red.	Chromium—dark bluish- grey. Vanadium—dark purplish- blue. Copper—purple. Cobalt—maroon. Uranium—maroon.

The foregoing azo-colouring matters when dyed on unmordanted wool are extremely sensitive to metals, this property being due, undoubtedly, to the ease with which the metallic lakes are produced.

The authors desire to express their thanks to the Research Grant Committees of the Royal Society and Chemical Society for grants which have partly defrayed the expenses of this investigation.

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*C.— $\beta$ -Naphthylmethylamine.*

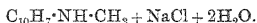
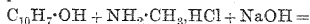
By GILBERT T. MORGAN and FREDERICK PAGE EVENS.

$\beta$ -NAPHTHYLMETHYLAMINE, the simplest alkyl derivative of  $\beta$ -naphthylamine, has not hitherto received detailed attention, probably owing to the circumstance that it is not produced readily by the action of ordinary methylating agents on the primary base.

Powerful methylating agents, such as methyl iodide in excess, lead to quaternary ammonium salts, from which the quaternary ammonium hydroxide and  $\beta$ -naphthyldimethylamine are successively obtained (Hantzsch, *Ber.*, 1880, **13**, 2054; Bamberger, *ibid.*, 1889,

22, 1306). By operating with equal weights of  $\beta$ -naphthylamine and methyl iodide at  $100^\circ$  in methyl-alcoholic solution, von Pechmann and Heinze produced a certain proportion of  $\beta$ -naphthylmethylamine, which, however, required purification by conversion into its nitrosoamine and subsequent reduction, so that the yield of recovered base was not satisfactory (*Ber.*, 1895, **28**, 2370; 1897, **30**, 1785). Pschorr and Karo subsequently obtained the base by the action of methyl sulphate on benzenesulphon- $\beta$ -naphthalide and subsequent hydrolysis of the product (*Ber.*, 1906, **39**, 3142).

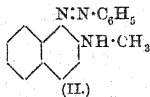
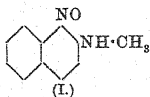
It has now been found that  $\beta$ -naphthylmethylamine can be prepared in excellent yield and in a state of purity by the interaction of  $\beta$ -naphthol and aqueous methylamine at high temperatures under pressure.



$\beta$ -Naphthol (100 grams), methylamine hydrochloride (75 grams), and 190 c.c. of 5*N*-sodium hydroxide were heated in a rotating steel autoclave at  $200$ – $220^\circ$  for seven hours, the pressure attained being about 21 kilos. per sq. cm. The oily contents of the autoclave were extracted successively with aqueous sodium hydroxide to remove unaltered  $\beta$ -naphthol, and with benzene to dissolve  $\beta$ -naphthylmethylamine. The benzene extract, after drying over calcium chloride, was distilled first under the ordinary and then under diminished pressure, the yield of secondary base being upwards of 80 per cent. of the theoretical.

$\beta$ -Naphthylmethylamine boiled at  $317^\circ/766$  mm. and at  $207^\circ/60$  mm., and when freshly distilled was colourless, but darkened rapidly on exposure to the air. It was identified by its solid nitrosoamine, which crystallised in pale yellow needles and melted at  $88^\circ$  (Pechmann gives  $90^\circ$ ; Pschorr and Karo,  $88$ – $89^\circ$ ).

1-Nitroso- $\beta$ -naphthylmethylamine (I).



$\beta$ -Naphthylmethylnitrosoamine (5 grams) was suspended in 20 c.c. of alcohol, and 20 c.c. of saturated alcoholic hydrogen chloride were slowly added with vigorous stirring at  $0^\circ$ . The nitrosoamine partly dissolved and the solution darkened. After twenty hours, a few dark green crystals had separated, and the mixture was poured into water. The hydrochloride of the nitroso-

base dissolved, whereas unaltered nitrosoamine was precipitated. On adding aqueous ammonia to the filtrate, the nitroso-base separated, and was crystallised from acetone, when it was obtained in dark green plates melting at  $142^{\circ}$ :

0.1041 gave 13.5 c.c.  $N_2$ \* at  $17^{\circ}$  and 753 mm.  $N=14.95$ .

$C_{11}H_{10}ON_2$  requires  $N=15.05$  per cent.

The optimum yield of 1-nitroso- $\beta$ -naphthylmethylamine obtained by the foregoing process was 75 per cent. of the theoretical. Unlike  $\beta$ -naphthylmethylnitrosoamine, this nitroso-base gave no Liebermann reaction. The conversion of 1-nitroso- $\beta$ -naphthylmethylamine into the anhydro-base (methenyl-1:2-naphthylene-diamine),  $C_{10}H_6 \begin{smallmatrix} \diagup N \\ \diagdown NH \end{smallmatrix} CH$ , did not proceed smoothly by the method of O. Fischer and Hepp, employed in the case of the ethenyl analogue (*Ber.*, 1887, 20, 2471), but when the nitroso-base was heated in alcoholic hydrogen chloride at  $100^{\circ}$  in a sealed tube, the hydrochloride of the anhydro-base separated in reddish-white crystals.

#### *Azo-derivatives of $\beta$ -Naphthylmethylamine.*

The azo-derivatives of  $\beta$ -naphthylmethylamine were prepared by two general methods, namely, (1) interaction of the base and diazonium salts, and (2) condensation of  $\beta$ -naphthylmethylnitrosoamine with primary aromatic amines.

#### *Benzeneazo- $\beta$ -naphthylmethylamine (II).*

The diazonium chloride from 1 gram of aniline was added in aqueous solution to  $\beta$ -naphthylmethylamine (1.7 grams) dissolved in cold dilute hydrochloric acid; a crimson coloration developed, and the addition of sodium acetate induced coagulation of the azo-compound. The viscid precipitate was dissolved in hot alcohol, from which the product crystallised in felted, scarlet needles melting at  $82-83^{\circ}$  (quantitative yield):

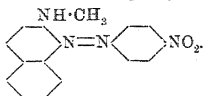
0.1176 gave 16.6 c.c.  $N_2$  at  $18^{\circ}$  and 750 mm.  $N=16.14$ .

$C_{17}H_{15}N_3$  requires  $N=16.09$  per cent.

Benzeneazo- $\beta$ -naphthylmethylamine was also obtained in satisfactory yield on warming a glacial acetic acid solution of  $\beta$ -naphthylmethylnitrosoamine and aniline in molecular proportions.

The product, which was precipitated on diluting the acetic acid solution with water, was identical with the foregoing preparation.

\* In this and the following nitrogen estimations the gas was measured over 33 per cent. aqueous potassium hydroxide.

*p*-Nitrobenzene-1-azo- $\beta$ -naphthylmethylamine,

An acid solution of *p*-nitrobenzenediazonium chloride (1 mol.) was added to  $\beta$ -naphthylmethylamine (1 mol.) dissolved in dilute hydrochloric acid, the temperature being below  $6^{\circ}$ . Sodium acetate precipitated the azo-compound in quantitative yield. The reddish-brown product was crystallised from ethyl acetate, acetone, benzene, or glacial acetic acid; it separated in matted, dark brown needles with bronze reflex, and melted at  $190-192^{\circ}$ :

0.0977 gave  $15.1$  c.c.  $N_2$  at  $15.5^{\circ}$  and  $750$  mm.  $N=17.85$ .

$C_{17}H_{14}O_2N_4$  requires  $N=18.30$  per cent.

*p*-Nitrobenzeneazo- $\beta$ -naphthylmethylamine was also produced by warming together in glacial acetic acid molecular proportions of *p*-nitroaniline and  $\beta$ -naphthylmethylnitrosoamine.

Like the preceding compound, this azo-derivative developed an intense violet coloration with concentrated sulphuric acid.

*Azo-dyes from  $\beta$ -Naphthylmethylamine.*

These azo-colouring matters can be obtained by the two general methods outlined in the foregoing preparations.

Diazo-derivative of amino-acid.	Tinctorial properties of the resulting dye.	Coloration in concentrated sulphuric acid.
1. Sulphanilic acid.	Scarlet on wool.	Reddish-blue.
2. Naphthionic acid.	Dark red on wool.	Dark violet.
3. Picramic acid : Direct dye. Dyed by metachrome process.	Dull purple on wool. After prolonged boiling (8 hours) a dark purple unlike the analogous dye from $\beta$ -naphthylamine, which changes to olive-green shades.	Reddish-brown.
4. Diaminostilbenedisul- phonic acid.	Purple on unmordanted cotton much bluer in shade than Hessian Purple N. from $\beta$ -naphthylamine.	Greenish-blue.

*Acyl Derivatives of  $\beta$ -Naphthylmethylamine.*

Aceto- $\beta$ -naphthylmethylamide,  $C_{10}H_7 \cdot N(CH_3) \cdot CO \cdot CH_3$ , was prepared by mixing  $\beta$ -naphthylmethylamine (1 mol.) and acetic

anhydride (1.5 mols.). The product when crystallised from light petroleum (b. p. 40—60°) separated in colourless, rhombic prisms melting at 50—51°:

0.1523 gave 9.6 c.c.  $N_2$  at 16° and 751.5 mm.  $N=7.28$ .

$C_{13}H_{13}ON$  requires  $N=7.04$  per cent.

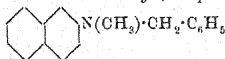
*Benzo- $\beta$ -naphthylmethylamide*,  $C_{10}H_7 \cdot N(CH_3) \cdot CO \cdot C_6H_5$ , produced by the Schotten-Baumann reaction, crystallised from light petroleum in colourless needles melting at 84°:

0.2663 gave 11.3 c.c.  $N_2$  at 20° and 762 mm.  $N=4.88$ .

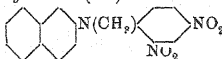
$C_{18}H_{15}ON$  requires  $N=5.36$  per cent.

*Toluene-p-sulphon- $\beta$ -naphthylmethylamide*.—This compound, which has already been described as resulting from the methylation of toluene-p-sulphon- $\beta$ -naphthylamide (Morgan and Micklethwait, T., 1912, 101, 150), was prepared more directly by grinding together  $\beta$ -naphthylmethylamine, toluene-p-sulphonyl chloride, and fused sodium acetate in approximately molecular proportions. The crude product, after digestion with aqueous sodium carbonate, was crystallised from alcohol, and separated in colourless, arborescent needles melting at 73° (T., 1912, *ibid.*, colourless needles, m. p. 77—78°).

*Benzyl- $\beta$ -naphthylmethylamine (III).*



(III.)



(IV.)

$\beta$ -Naphthylmethylamine (1 mol.) and benzyl chloride (1.25 mols.) were mixed and heated with 10 per cent. aqueous sodium hydroxide (1.25 mols.) in a reflux apparatus for several hours until the solid product of the mixture of the two organic reagents had been decomposed. On cooling, a brown, solid mass separated consisting of crude benzyl- $\beta$ -naphthylmethylamine (yield, 70 per cent.). This base was soluble in benzene, acetone, or alcohol, and crystallised in lustrous, colourless needles melting at 82—83°:

0.3358 gave 15.8 c.c.  $N_2$  at 17° and 765 mm.  $N_1=5.51$ .

$C_{18}H_{17}N$  requires  $N=5.67$  per cent.

Like all the other known dialkyl- $\beta$ -naphthylamines, this tertiary base did not couple with diazonium salts.

*2:4-Dinitrophenyl- $\beta$ -naphthylmethylamine (IV).*

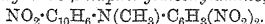
Molecular proportions of  $\beta$ -naphthylmethylamine and 4-chloro-1:3-dinitrobenzene were dissolved in alcohol, and the solution was

heated under reflux with fused sodium acetate for two to three hours. The crystalline product separating from the cooled solution was washed successively with alcohol and water to remove 4-chloro-1:3-dinitrobenzene and sodium salts respectively. The final residue was crystallised from benzene or acetic acid, from which it separated in orange-red, elongated prisms melting at  $183^{\circ}$ :

0.1630 gave 18.2 c.c.  $N_2$  at  $18^{\circ}$  and 756 mm.  $N=12.88$ .

$C_{17}H_{13}O_4N_3$  requires  $N=13.00$  per cent.

2:4-Dinitrophenylnitro- $\beta$ -naphthylmethylamine,



—The preceding dinitro-compound was dissolved in the least possible amount of glacial acetic acid and treated with sufficient nitric acid (D 1.42), diluted with an equal volume of glacial acetic acid, to introduce one nitro-group. The solution was stirred thoroughly, warmed, and left overnight in the ice-chest, when a mass of yellow crystals separated. This product crystallised from alcohol in yellow flakes and melted at  $156-157^{\circ}$ :

0.1080 gave 14.7 c.c.  $N_2$  at  $22^{\circ}$  and 761 mm.  $N=15.52$ .

$C_{17}H_{12}O_6N_4$  requires  $N=15.22$  per cent.

The authors' thanks are due to the British Dyestuffs Corporation (Manchester) for the starting materials employed in this investigation.

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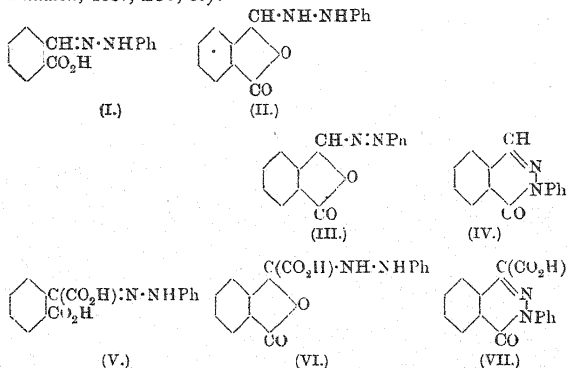
### CI.—Action of Phenylhydrazine on Phthalaldehydic and Phthalonic Acids: Phenyl-hydrazo- and Azo-Phthalide.

By PRAFULLA CHANDRA MITTER and JNANENDRA NATH SEN.

In a previous communication (T., 1917, 111, 988) the authors have shown that by the action of phenylhydrazine on opianic and nitro-opianic acids in ethereal solution derivatives of hydrazophthalide are formed, which can be oxidised by mercuric oxide to azo-phthalides. In the case of phthalonic acid definite indications of the formation of hydrazo- and azo-phthalide derivatives were obtained, although the products could not then be isolated. It has

now been found that on adding a solution of phenylhydrazine hydrochloride to a nearly neutral solution of phthalonic acid the phenylhydrazone is obtained, which on treatment with dilute hydrochloric acid is converted into phenylphthalazonecarboxylic acid identical with the anhydrophenylhydrazine-*o*-carboxyphenylglyoxylic acid prepared by Henriques (*Ber.*, 1888, **21**, 1610).

In the case of phthalaldehydic acid, treatment with phenylhydrazine hydrochloride under similar conditions gives phenylhydrazophthalide, which can be oxidised in acetone solution by mercuric acetamide to phenylazophthalide. Treatment with acetic acid converts the hydrazophthalide into phenylphthalazone (Racine, *Annalen*, 1887, **239**, 80):



#### EXPERIMENTAL.

##### *Phenylhydrazone of Phthalaldehydic Acid (I).*

On account of the great solubility of the phenylhydrazine derivative in ether, the compound was prepared by the action of phenylhydrazine hydrochloride on the sodium salt of phthalaldehydic acid.

Phthalaldehydic acid (1.5 grams: 1 mol.) was dissolved in sodium carbonate solution (0.75 mol.), and to this an aqueous solution of phenylhydrazine hydrochloride (1.45 grams: 1 mol.) was added. The phenylhydrazine derivative separated almost immediately as a canary-yellow powder in almost quantitative yield (2.7 grams). On crystallisation from slightly warm dilute alcohol it was obtained in pale yellow needles melting at 106°, which turned pink on exposure

to air. It dissolves readily in sodium hydrogen carbonate solution or ammonia. Acetic acid transforms it into the cyclic compound:

0.1065 gave 0.2741  $\text{CO}_2$  and 0.0476  $\text{H}_2\text{O}$ .  $\text{C}=70.19$ ;  $\text{H}=4.97$ .

0.1011 „ 10.3 c.c.  $\text{N}_2$  at  $24^\circ$  and 760 mm.  $\text{N}=11.79$ .

$\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_2$  requires  $\text{C}=70.00$ ;  $\text{H}=5.00$ ;  $\text{N}=11.66$  per cent.

The substance was dissolved in alcohol and titrated with standard alkali. It was found to be monobasic:

0.1373 required 5.65 c.c. of  $\text{N}/10$ -alkali, whilst this weight of a monobasic acid of the above formula requires 5.70 c.c.

### *Phenylazophthalide.*

Phenylhydrazophthalide (II, 0.55 gram) was dissolved in about 20 c.c. of pure acetone, 2 grams of pure recrystallised mercuric acetamide were added, and the mixture was heated on the water-bath under reflux for about three hours. The colour of the solution gradually changed to deep yellow. The solution was filtered, the residue washed with acetone, and the washings added to the filtrate. The filtrate was evaporated to dryness and the residue washed with dilute sodium carbonate solution and water, and then dissolved in acetone. On adding water a small quantity of tarry matter was precipitated, which was removed by filtration. Further addition of water precipitated the azo-compound (III) in yellow plates melting at  $149\text{--}150^\circ$ . The substance is insoluble in sodium carbonate, and gives with concentrated sulphuric acid a purple coloration. The alcoholic solution is yellow with a green shade, and the colour changes to pink on the addition of alkali.

The compound dissolves readily in acetone or benzene:

0.1581 gave 0.4132  $\text{CO}_2$  and 0.0612  $\text{H}_2\text{O}$ .  $\text{C}=71.05$ ;  $\text{H}=4.30$ .

0.1025 „ 10.5 c.c.  $\text{N}_2$  at  $24^\circ$  and 760 mm.  $\text{N}=11.86$ .

$\text{C}_{14}\text{H}_{10}\text{O}_2\text{N}_2$  requires  $\text{C}=70.49$ ;  $\text{H}=4.20$ ;  $\text{N}=11.77$  per cent.

### *Phenylphthalazone (IV).*

Phenylhydrazophthalide is warmed with a small quantity of glacial acetic acid for a few minutes and hot water is added. The phthalazone is readily obtained in fine needles with a pale pink colour melting at  $105^\circ$ . It is insoluble in alkali even on boiling. (Found:  $\text{N}=13.11$ .  $\text{C}_{14}\text{H}_{10}\text{ON}_2$  requires  $\text{N}=12.61$  per cent.)

### *Phthalonic Acid and Phenylhydrazine.*

Phthalonic acid (1 gram: 1 mol.) was dissolved in water containing sodium carbonate (0.42 gram: 0.75 mol.), and a solution of



phenylhydrazine hydrochloride (1·5 grams: 2 mols.) in water was added. The phenylhydrazine derivative (V or VI) separated at once in crystalline flakes melting at 171—172°. It dissolves readily in acetone or alcohol, but on the addition of water the solution deposits an oil. All attempts at recrystallisation failed:

0·0938 gave 0·2167 CO<sub>2</sub> and 0·0360 H<sub>2</sub>O. C=63·06; H=4·27.

0·1169 „ 9·6 c.c. N<sub>2</sub> at 23° and 760 mm. N=9·73.

C<sub>15</sub>H<sub>12</sub>O<sub>4</sub>N<sub>2</sub> requires C=63·38; H=4·23; N=9·85 per cent.

The substance was dissolved in dilute alcohol and titrated with standard alkali. It was found to be dibasic:

0·1449 required 9·4 c.c. of *N*/10-alkali, whilst this weight of a dibasic acid of the above molecular formula requires 10·2 c.c.

The substance gradually turns brownish-yellow on exposure to air. Attempts at oxidation with mercuric acetamide did not yield any pure product.

#### *Phenylphthalazonecarboxylic Acid (VII).*

The mother liquor after the filtration of the hydrazo-compound deposits, on keeping, long needles with a silky lustre dissolving readily in sodium carbonate solution and melting at 210°. The same substance is also obtained by keeping the hydrazophthalidecarboxylic acid suspended in dilute hydrochloric acid. (Found, C=67·08; H=3·63; N=10·10. C<sub>15</sub>H<sub>10</sub>O<sub>3</sub>N<sub>2</sub> requires C=67·67; H=3·76; N=10·05 per cent.

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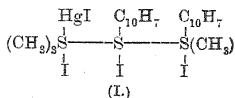
### CII.—Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. Part VII. Chain Compounds of Sulphur (continued).

By SIR PRAFULLA CHANDRA RÂY and PRAFULLA CHANDRA GUHA.

IN Part IV. of this series (this vol., p. 261), among the products of the interaction of phenyl mercaptan and mercuric nitrite which were isolated, was one having the empirical formula Ph<sub>2</sub>S<sub>3</sub>Hg. When  $\alpha$ -naphthyl mercaptan is treated with mercuric nitrite only one product is obtained, which is the exact analogue of the former, namely, (C<sub>10</sub>H<sub>7</sub>)<sub>2</sub>S<sub>3</sub>Hg. This, like the benzenoid derivative, is

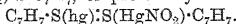
soluble in hot benzene, and can therefore be easily obtained in a state of purity.

The action of methyl iodide on the compound  $\text{Ph}_2\text{S}_3\text{Hg}$  leads to a trisulphonium compound in which all the sulphur atoms are quadrivalent (compare Part IV.). The action of alkyl iodides on the new compound,  $(\text{C}_{10}\text{H}_7)_2\text{S}_3\text{Hg}$ , has proved to be of much interest. With methyl iodide, for instance, three sulphonium derivatives, tri-, di-, and mono-, are formed together. The trisulphonium compound (I) contains two sexavalent and one quadrivalent sulphur atoms. The



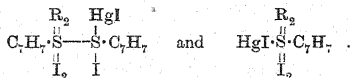
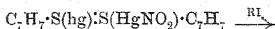
monosulphonium derivative also contains a sexavalent sulphur atom, and all the monosulphonium compounds described in the present paper are of this category.

The action of *p*-tolyl mercaptan on mercuric nitrite has also been studied. The mercaptide nitrite corresponds with the formula  $\text{C}_7\text{H}_7 \cdot \text{S}(\text{hg})(\text{HgNO}_2) \cdot \text{S} \cdot \text{C}_7\text{H}_7$ , or preferably

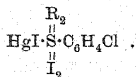


*p*-Chlorophenyl mercaptan also yields a compound of exactly the same type. That they are definite compounds is proved by the fact that successive crops from hot benzene solution have the same melting point and composition.

The mercaptide nitrite obtained from *p*-tolyl mercaptan reacts with methyl and ethyl iodides, yielding in each case a mono- and a di-sulphonium compound, the sulphur atoms of the latter being sexavalent (compare Part VI., this vol., p. 548):



The mercaptide nitrite from *p*-chlorophenyl mercaptan gives with alkyl iodides only one monosulphonium compound of the type:



In Part VI. of this series one of us has described disulphonium compounds containing one or both of the atoms of sulphur in the

sexavalent condition. The present work not only corroborates the existence of this class of compounds, but goes a step further in that a trisulphonium compound is described containing two sexavalent and one quadrivalent sulphur atoms.

In addition to the monosulphonium compounds described in the present paper, another series has been prepared, namely, that obtained by the reaction of ethyl sulphide and mercuric iodide with the higher and lower homologues of ethyl iodide, and in each case a compound of the type  $\text{Et}_2\text{S}\cdot\text{RI}\cdot\text{HgI}_2$  has been obtained (compare Smiles and Hilditch, T., 1907, 91, 1396).

It has already been shown that the disulphonium compounds can be synthesised by the direct union of the components, for example, ethyl disulphide, ethyl iodide, and mercuric iodide (T., 1916, 109, 611). By substituting, however, the other alkyl iodides the corresponding members of the series have been obtained, with this difference, that an interchange of radicles invariably takes place. Thus, when a mixture of ethyl disulphide and mercuric iodide is treated with an alkyl iodide, RI, compounds of the type  $\text{EtRS}_2\cdot\text{HgI}_2\cdot\text{RI}$  are formed. Again, when a mercaptide nitrite like the compound  $\text{EtS}\cdot\text{HgNO}_2$  is treated with an alkyl iodide, RI, by an interchange of radicles, the compound  $\text{EtRS}_2\cdot\text{HgI}_2\cdot\text{RI}$  is obtained (*loc. cit.*). It is thus seen that either mode of formation yields the same compound, the interchange of radicles being thus the most prominent feature. There is, however, this marked difference that in the monosulphonium series no such interchange of radicles has been found to take place.

#### EXPERIMENTAL.

##### *Interaction of $\alpha$ -Naphthyl Mercaptan and Mercuric Nitrite:*

##### *Formation of the Compound $(\text{C}_{10}\text{H}_7)_2\text{S}_3\text{Hg}$ .*

An alcoholic solution of  $\alpha$ -naphthyl mercaptan was slowly dropped from a pipette into mercuric nitrite solution with constant shaking. At first a white precipitate appeared, which, however, soon acquired a yellow tint. The granular precipitate was collected, washed, and dried in a vacuum. For further purification it was crystallised from boiling benzene, in which it was fairly readily soluble, and then melted at  $198^\circ$ :

0.1118 gave 0.1827  $\text{CO}_2$  and 0.0344  $\text{H}_2\text{O}$ .  $\text{C}=44.57$ ;  $\text{H}=3.43$ .

0.1200 ,, 0.0459 Hg and 0.1354  $\text{BaSO}_4$ .  $\text{Hg}=37.93$ ;  $\text{S}=15.38$ .

$\text{C}_{20}\text{H}_{14}\text{S}_3\text{Hg}$  requires  $\text{C}=43.63$ ;  $\text{H}=2.54$ ;  $\text{Hg}=36.36$ ;

$\text{S}=17.45$  per cent.

*Interaction of the Compound  $(C_{10}H_7)_2S_3Hg$  and Methyl Iodide:  
Formation of the Trisulphonium Compound (I).*

The method of procedure is exactly the same as in the interaction of simple mercaptide nitrites and alkyl iodides. After heating with methyl iodide under reflux, the mixture was allowed to cool. Within half an hour, the heavy, oily liquid at the bottom began to solidify to well-defined crystals, which were collected. The substance was insoluble in acetone, and was therefore washed several times with this solvent. Finally, it was recrystallised from hot methyl alcohol, when dull yellow crystals melting at  $113^\circ$  were obtained. Both the soluble and insoluble varieties of this series of sulphonium compounds dissolve readily in boiling methyl alcohol, and thus all of them have been obtained in a pure condition:

0.2196 gave 0.2219  $CO_2$  and 0.0574  $H_2O$ .  $C=27.56$ ;  $H=2.90$ .  
0.3016 „ 0.0540 Hg „ 0.2484 AgI.  $Hg=17.91$ ;  $I=44.15$ .  
0.3729 „ 0.2223  $BaSO_4$ .  $S=8.19$ .

$C_{26}H_{32}I_4S_3Hg$  requires  $C=27.18$ ;  $H=2.79$ ;  $Hg=17.42$ ;  
 $I=44.26$ ;  $S=8.36$  per cent.

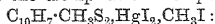
The filtrate, after the separation of the above insoluble compound, was freed from excess of methyl iodide by evaporation. The oily residue was dissolved in acetone, the solution filtered, concentrated to a small bulk, and excess of ether added, when a yellow oil was again precipitated. The oil was dissolved in boiling methyl alcohol, and on slowly cooling, yellow needles with a faint green tint separated. From the methyl alcoholic solution five successive crops were obtained by fractional crystallisation. Of these, the first two crops melted at  $102^\circ$ ; they were therefore mixed and again crystallised from the above solvent, when the product melted at the same temperature. This was the sexavalent monosulphonium compound and gave the following results on analysis:

0.1496 gave 0.1058  $CO_2$  and 0.0284  $H_2O$ .  $C=19.29$ ;  $H=2.11$ .  
0.3927 „ 0.1023 Hg „ 0.3524 AgI.  $Hg=26.05$ ;  $I=48.48$ .  
0.2650 „ 0.0693 Hg.  $Hg=26.12$ .

$C_{12}H_{13}I_3SHg$  requires  $C=18.7$ ;  $H=1.82$ ;  $Hg=25.97$ ;  
 $I=49.5$  per cent.

The mother liquor from which the above five fractions were obtained began to deposit oily globules which were dissolved in acetone. On the addition of ether an oil was obtained which was kept in a vacuum over sulphuric acid for several days, but did not solidify. On stirring, however, with a little ether, crystallisation at once occurred. The compound was now purified by repeated crystal-

lisation from methyl alcohol, and when pure it melted sharply at 93°. It consisted of the disulphonium compound,



0.2020 gave 0.1418  $\text{CO}_2$  and 0.0332  $\text{H}_2\text{O}$ .  $\text{C}=19.14$ ;  $\text{H}=1.82$ .

0.2055 „ 0.0507 Hg „ 0.1750 AgI.  $\text{Hg}=24.67$ ;  $\text{I}=46.02$ .

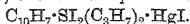
$\text{C}_{10}\text{H}_7\text{I}_3\text{S}_2\text{Hg}$  requires  $\text{C}=17.95$ ;  $\text{H}=1.52$ ;  $\text{Hg}=24.93$ ;

$\text{I}=47.51$  per cent.

As was to be expected, an interchange of radicle takes place in this case.

*Interaction of the Compound  $(\text{C}_{10}\text{H}_7)_2\text{S}_3\text{Hg}$  and Propyl Iodide:*

*Formation of the Monosulphonium Compound,*



From methyl-alcoholic solution the compound was deposited as an oil which, when kept in a vacuum for a week, solidified. It was then further purified by recrystallisation from methyl alcohol, when it melted at 106°:

0.1345 gave 0.1173  $\text{CO}_2$  and 0.0334  $\text{H}_2\text{O}$ .  $\text{C}=23.82$ ;  $\text{H}=2.76$ .

0.3701 „ 0.0900 Hg „ 0.3101 HgI.  $\text{Hg}=24.32$ ;  $\text{I}=45.28$ .

$\text{C}_{16}\text{H}_{21}\text{I}_3\text{SHg}$  requires  $\text{C}=23.25$ ;  $\text{H}=2.54$ ;  $\text{Hg}=24.21$ ;

$\text{I}=46.13$  per cent.

*Mercuric Nitrite and p-Tolyl Mercaptan: Formation of the Compound  $\text{C}_7\text{H}_7\cdot\text{S}(\text{hg})\cdot\text{S}(\text{HgNO}_2)\cdot\text{C}_7\text{H}_7$ .*

On adding an alcoholic solution of the mercaptan to the mercuric nitrite solution a product is obtained which on allowing to remain and occasionally stirring forms a dull yellow, granular mass. This is purified by crystallisation from hot benzene. Three successive crops melted at 127°. The purity of the compound is thus unquestionable. It evolves nitrous fumes when treated with hydrochloric acid:

0.0937 gave 0.0982  $\text{CO}_2$  and 0.0234  $\text{H}_2\text{O}$ .  $\text{C}=28.58$ ;  $\text{H}=2.77$ .

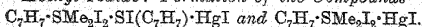
0.1419 „ 3.2 c.c.  $\text{N}_2$  at 25° and 760 mm.  $\text{N}=2.43$ .

0.1316 „ 0.0737 HgS.  $\text{Hg}=48.27$ .

$\text{C}_{28}\text{H}_{28}\text{O}_4\text{N}_2\text{S}_4\text{Hg}_3$  requires  $\text{C}=28.38$ ;  $\text{H}=2.36$ ;  $\text{N}=2.36$ ;

$\text{Hg}=50.68$  per cent.

*Interaction of the Mercaptide Nitrite of p-Tolyl Mercaptan and Methyl Iodide: Formation of the Compounds*



A clear solution was obtained in this case on digesting the mercaptide nitrite with methyl iodide for three or four minutes. After

evaporating the excess of methyl iodide the oily residue was dissolved in acetone and the solution filtered. On concentrating and cooling, a small quantity of yellowish-white, scaly crystals began to be deposited. The compound was collected and washed with a small quantity of cold acetone. On recrystallising from hot methyl alcohol it melted sharply at  $109^{\circ}$ . The filtrate on evaporation of the acetone, left an oily residue, which was dissolved in methyl alcohol. On slow evaporation of the solvent, needle-shaped, yellow crystals melting at  $121^{\circ}$  were obtained.

The *disulphonium* compound melting at  $109^{\circ}$  gave the following results on analysis:

0.1656 gave 0.1215  $\text{CO}_2$  and 0.0428  $\text{H}_2\text{O}$ .  $\text{C}=20.08$ ;  $\text{H}=2.87$ .

0.3418 „ 0.0735 Hg „ 0.2950 AgI.  $\text{Hg}=21.50$ ;  $\text{I}=46.63$ .

$\text{C}_{16}\text{H}_{20}\text{I}_4\text{S}_2\text{Hg}$  requires  $\text{C}=19.51$ ;  $\text{H}=2.03$ ;  $\text{Hg}=20.32$ ;

$\text{I}=51.63$  per cent.

The *monosulphonium* compound melting at  $121^{\circ}$  gave the following results:

0.2718 gave 0.1440  $\text{CO}_2$  and 0.0686  $\text{H}_2\text{O}$ .  $\text{C}=14.45$ ;  $\text{H}=2.80$ .

0.4152 „ 0.1132 Hg „ 0.3912 AgI.  $\text{Hg}=27.27$ ;  $\text{I}=50.91$ .

$\text{C}_9\text{H}_{13}\text{I}_3\text{SHg}$  requires  $\text{C}=14.51$ ;  $\text{H}=1.75$ ;  $\text{Hg}=27.25$ ;

$\text{I}=51.90$  per cent.

*Interaction of the Mercaptide Nitrite of p-Tolyl Mercaptan and Ethyl Iodide: Formation of the Compounds*

$\text{C}_7\text{H}_7\cdot\text{SEt}_2\text{I}_2\cdot\text{SI}(\text{C}_7\text{H}_7)\cdot\text{HgI}$  and  $\text{C}_2\text{H}_5\cdot\text{C}_6\text{H}_4\cdot\text{SEt}_2\text{I}_2\cdot\text{HgI}$ .

The method of procedure was exactly the same as described above. The *disulphonium* compound melts at  $120^{\circ}$ :

0.1235 gave 0.0240 Hg and 0.1111 AgI.  $\text{Hg}=19.43$ ;  $\text{I}=48.63$ .

$\text{C}_{18}\text{H}_{24}\text{I}_4\text{S}_2\text{Hg}$  requires  $\text{Hg}=19.76$ ;  $\text{I}=50.20$  per cent.

The *monosulphonium* compound melts at  $70^{\circ}$ :

0.1387 gave 0.0946  $\text{CO}_2$  and 0.0320  $\text{H}_2\text{O}$ .  $\text{C}=18.60$ ;  $\text{H}=2.54$ .

0.2943 „ 0.0746 Hg „ 0.2641 AgI.  $\text{Hg}=25.70$ ;  $\text{I}=48.50$ .

$\text{C}_{12}\text{H}_{19}\text{I}_3\text{SHg}$  requires  $\text{C}=18.50$ ;  $\text{H}=2.44$ ;  $\text{Hg}=25.77$ ;

$\text{I}=49.09$  per cent.

*Interaction of the Mercaptide Nitrite of p-Tolyl Mercaptan and Propyl Iodide: Formation of the Monosulphonium Compound,*

$\text{C}_7\text{H}_7\cdot\text{SI}_2(\text{C}_3\text{H}_7)_2\cdot\text{HgI}$ .

In this case also (compare p. 1151) the compound could not be brought into the solid condition until it had been kept in a vacuum

desiccator for some days. Finally, it was crystallised from methyl alcohol, when it melted at  $71^{\circ}$ :

0.1670 gave 0.1193  $\text{CO}_2$  and 0.0425  $\text{H}_2\text{O}$ .  $\text{C}=19.48$ ;  $\text{H}=2.83$ .

0.3006 „ 0.0764 Hg and 0.2520 AgI.  $\text{Hg}=25.42$ ;  $\text{I}=45.30$ .

$\text{C}_{13}\text{H}_{21}\text{I}_3\text{SHg}$  requires  $\text{C}=19.75$ ;  $\text{H}=2.66$ ;  $\text{Hg}=25.32$ ;

$\text{I}=48.23$  per cent.

*Interaction of p-Chlorophenyl Mercaptan and Mercuric Nitrite:  
Formation of the Compound  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{S}(\text{hg})\cdot\text{S}(\text{HgNO}_2)\cdot\text{C}_6\text{H}_4\text{Cl}$ .*

This compound was crystallised from boiling benzene solution:

0.3576 gave 0.1662 Hg and 0.1600 AgCl.  $\text{Hg}=46.47$ ;  $\text{Cl}=11.07$ .

$\text{C}_{24}\text{H}_{16}\text{O}_4\text{N}_2\text{Cl}_4\text{Hg}_3$  requires  $\text{Hg}=47.39$ ;  $\text{Cl}=11.22$  per cent.

*Interaction of the Mercaptide Nitrite of p-Chlorophenyl Mercaptan  
and Methyl Iodide: Formation of the Compound  
 $\text{C}_6\text{H}_4\text{Cl}\cdot\text{SMe}_2\text{I}_2\cdot\text{HgI}$ .*

This crystallised from hot methyl alcohol in yellow needles melting at  $139^{\circ}$ :

0.2647 gave 0.1202  $\text{CO}_2$  and 0.0400  $\text{H}_2\text{O}$ .  $\text{C}=12.38$ ;  $\text{H}=1.68$ .

0.3591 „ 0.0945 Hg, 0.4118 AgI + AgCl, and 0.2863 AgCl by chlorination.  $\text{Hg}=26.32$ ;  $\text{I}=48.47$ ;  $\text{Cl}=6.19$ .

$\text{C}_8\text{H}_{10}\text{ClI}_3\text{SHg}$  requires  $\text{C}=12.73$ ;  $\text{H}=1.33$ ;  $\text{Hg}=26.51$ ;

$\text{I}=50.49$ ;  $\text{Cl}=4.70$  per cent.

The corresponding *ethyl* compound was at first deposited as an oil, but, when purified by repeated crystallisation, formed a yellow powder melting at  $64^{\circ}$ :

0.2796 gave 0.1446  $\text{CO}_2$  and 0.0495  $\text{H}_2\text{O}$ .  $\text{C}=14.11$ ;  $\text{H}=1.77$ .

0.4310 „ 0.1100 Hg, 0.4506 AgI + AgCl, and 0.3051 AgCl by chlorination.  $\text{Hg}=25.52$ ;  $\text{I}=46.83$ ;  $\text{Cl}=4.42$ .

$\text{C}_{10}\text{H}_{14}\text{ClI}_3\text{SHg}$  requires  $\text{C}=15.34$ ;  $\text{H}=1.79$ ;  $\text{Hg}=25.57$ ;

$\text{I}=48.71$ ;  $\text{Cl}=4.54$  per cent.

*Reaction of Ethyl Sulphide and Mercuric Iodide with Alkyl Iodides.*

A mixture of ethyl sulphide and ethyl iodide was heated under reflux with an excess of mercuric iodide, when a golden-yellow liquid was obtained. It was dissolved in a minimum quantity of acetone and precipitated by ether and the process repeated. A yellow, crystalline powder was obtained, which melted at  $110^{\circ}$ . A small quantity remained insoluble in acetone and melted at  $146\text{--}147^{\circ}$  (com-

pare Part VI). The compound melting at  $110^{\circ}$  gave the following results:

0.1984 gave 0.0757  $\text{CO}_2$  and 0.0427  $\text{H}_2\text{O}$ .  $\text{C}=10.41$ ;  $\text{H}=2.39$ .

0.2775 „ 0.0764  $\text{Hg}$  „ 0.2708  $\text{AgI}$ .  $\text{Hg}=27.53$ ;  $\text{I}=52.74$ .

$\text{C}_8\text{H}_{15}\text{I}_3\text{SHg}$  requires  $\text{C}=10.29$ ;  $\text{H}=2.14$ ;  $\text{Hg}=28.57$ ;  
 $\text{I}=54.43$  per cent.

A mixture of ethyl sulphide and methyl iodide was treated with excess of mercuric iodide as above. The yellow, crystalline product melted at  $65-67^{\circ}$ :

0.2652 gave 0.0862  $\text{CO}_2$  and 0.052  $\text{H}_2\text{O}$ .  $\text{C}=8.86$ ;  $\text{H}=2.180$ .

0.5518 „ 0.1595  $\text{Hg}$  „ 0.5347  $\text{AgI}$  and 0.1480  $\text{BaSO}_4$ .  $\text{Hg}=28.91$ ;  $\text{I}=52.36$ ;  $\text{S}=3.68$ .

$\text{C}_5\text{H}_{13}\text{I}_3\text{SHg}$  requires  $\text{C}=8.75$ ;  $\text{H}=1.90$ ;  $\text{Hg}=29.15$ ;  $\text{I}=55.53$ ;  
 $\text{S}=4.67$  per cent.

The corresponding yellow, crystalline *propyl* derivative melted at  $88-89^{\circ}$ :

0.1904 gave 0.0861  $\text{CO}_2$  and 0.0480  $\text{H}_2\text{O}$ .  $\text{C}=12.33$ ;  $\text{H}=2.81$ .

0.3796 „ 0.1038  $\text{Hg}$  „ 0.3569  $\text{AgI}$ .  $\text{Hg}=27.35$ ;  $\text{I}=50.83$ .

$\text{C}_7\text{H}_{17}\text{I}_3\text{SHg}$  requires  $\text{C}=11.77$ ;  $\text{H}=2.38$ ;  $\text{Hg}=28.00$ ;  
 $\text{I}=53.36$  per cent.

The corresponding yellow, crystalline *butyl* derivative melted at  $72-73^{\circ}$ :

0.3829 gave 0.1874  $\text{CO}_2$  and 0.0673  $\text{H}_2\text{O}$ .  $\text{C}=13.35$ ;  $\text{H}=1.95$ .

0.5745 „ 0.1565  $\text{Hg}$ .  $\text{Hg}=27.24$ .

$\text{C}_8\text{H}_{19}\text{I}_3\text{SHg}$  requires  $\text{C}=13.19$ ;  $\text{H}=2.61$ ;  $\text{Hg}=27.47$  per cent.

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### CHII.—*Asymmetric Replacement in the meta-Series.* *Part I.*

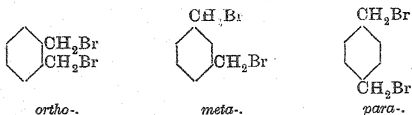
By WILLIAM HENRY GOUGH and JOCELYN FIELD THORPE.

THE interaction of organic halogen derivatives containing two atoms of the halogen and substances of the type of potassium cyanide usually leads to the replacement of both halogen atoms and the consequent production of the corresponding dinitriles. If an insufficient quantity of potassium cyanide is present completely to effect this change, it generally happens that the whole of the cyanide is utilised in forming the dinitriles and the rest of the

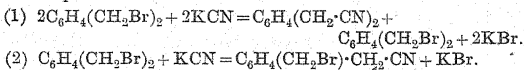


dihalogen derivatives remains unaltered. This is, at any rate, the usual course of the reaction when the halogen atoms are symmetrically placed in the organic molecule, although it is obvious that asymmetric substitution, that is, the successive replacement of the halogen atoms, with the intermediate formation of the compound in which only one halogen atom is substituted, can and does take place when the halogen atoms are in positions in the organic molecule which cause them to possess different degrees of reactivity, and therefore render one of them more open to attack than the other.

There is thus no reason to suppose that the three  $\omega\omega'$ -dibromoxylens (xylylene dibromides), in each of which the bromine atoms



are symmetrically placed to each other, would exhibit any fundamental differences in their behaviour towards alcoholic potassium cyanide under the same experimental conditions, and yet the evidence brought forward in this communication shows clearly that whereas the *o*- and *p*-compounds are converted directly into the dinitriles without any intermediate formation of the bromonitriles,  $C_6H_4(CH_2Br) \cdot CH_2 \cdot CN$ —even though an insufficient quantity of potassium cyanide to form the dinitrile is present—the bromine atoms in the meta-compound can be easily replaced successively, and that it is a simple matter to prepare the *m*-bromo-nitrile, of the above formula, in considerable quantities. In other words, the reaction between  $\omega\omega'$ -dibromo-*o*-(or *p*-)xylene and alcoholic potassium cyanide (equal molecules) is represented by equation (1), whereas equation (2) represents the reaction in the case of the meta-compound:



It is certainly remarkable that this property of the meta-compound should have been hitherto unrecognised, because the conversion of all three  $\omega\omega'$ -dibromoxylens into the nitriles has been carried out by several investigators. Indeed, it was while we were attempting to prepare the *m*-dinitrile by what we understood to be Kipping's method that the isolation of this intermediate product occurred. It happens that the reference to Kipping's paper is quoted wrongly in "Beilstein," and the details of the preparation given there, which are evidently taken from the paper by Oddo

(*Gazzetta*, 1893, **23**, ii, 338), state that twenty hours on the water-bath are sufficient to convert 13.4 grams of  $\omega\omega'$ -dibromo-*m*-xylene, 9 grams of potassium cyanide, and 500 c.c. of alcohol completely into the dinitrile and potassium bromide. As a matter of fact, in our hands these conditions led to a 90 per cent. yield of the pure *m*-bromo-nitrile, and we were unable to isolate any trace of the dinitrile. A subsequent reference to Kipping's paper (T., 1888, **53**, 41) showed that he had heated his reaction mixture on the water-bath for a "considerable time." It is certain, moreover, that Kipping's product could not have contained any appreciable quantity of the bromo-nitrile, because he found that the crude oil formed in his reaction gave an almost theoretical yield of *m*-phenylenediacetic acid when it was hydrolysed by alcoholic potassium hydroxide (*ibid.*, p. 43).

It seemed therefore desirable to carry out a series of comparative experiments on the behaviour of the three  $\omega\omega'$ -dibromoxylenes towards potassium cyanide under different conditions in order to ascertain whether this property of asymmetric replacement was characteristic of the meta-series, and whether, in fact, we had to hand another example of abnormal behaviour in these derivatives.

$\omega\omega'$ -Dibromo-*o*-xylene has been converted into the dinitrile by Baeyer and Pape (*Ber.*, 1884, **17**, 447); similar conditions were subsequently employed by Moore and Thorpe (T., 1908, **93**, 175) for the preparation of large quantities of the compound. When 10 per cent. more than the amount of potassium cyanide, representing two molecular proportions, is used and the quantity of the solvent is reduced to a minimum, the reaction proceeds smoothly and is finished at the end of an hour, the heat generated being sufficient to carry the change to completion.

The yield is good, and the only by-product accompanying the dinitrile is a small quantity of oily impurity of indefinite character; no trace of the bromo-nitrile can be detected.

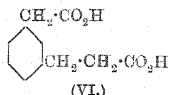
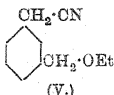
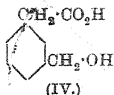
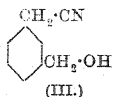
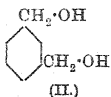
The interaction of one molecular proportion of  $\omega\omega'$ -dibromo-*o*-xylene and one of potassium cyanide was investigated by Moore and Thorpe during the earlier experiments (*loc. cit.*), but the details were not then published, because the preparation of the intermediate bromo-nitrile, which was the object in view, was not achieved. A description of this work is now included in the experimental portion of this paper; it shows clearly that the reaction proceeds in accordance with equation (1) above.

*p*-Phenylenediacetonitrile has been prepared by Klippert (*Ber.*, 1876, **9**, 1766) from  $\omega\omega'$ -dichloro-*p*-xylene, and by Kipping (T., 1888, **53**, 44) from the corresponding dibromo-derivative. Kipping found that the yield of the dinitrile was only approximately 50 per

cent. of the theoretical, the remainder of the product being an amorphous substance of resinous character; we agree with him that it does not appear possible to avoid the formation of this resin or to increase the yield of the dinitrile by varying the conditions. The reaction under his conditions proceeds smoothly, but requires a longer time than is the case with the ortho-derivative; no trace of the bromo-nitrile is formed.

When one molecular proportion of  $\omega\omega'$ -dibromo-*p*-xylene and one of potassium cyanide are employed, the reaction proceeds in accordance with equation (1), approximately 50 per cent. of the dibromo-compound being recovered unchanged and the remainder being converted into the dinitrile.

The references in connexion with the preparation of *m*-phenylenediacetonitrile have already been given, and we have stated that, in our hands, the published experimental conditions led to the formation of the *m*-bromo-nitrile (I) as sole product. The constitution of this substance has been placed beyond question by its conversion into the already known  $\omega\omega'$ -dihydroxy-*m*-xylene (II) (Colson, *Ann. Chim. Phys.*, 1885, [vi], 6, 112) by the action of freshly precipitated silver hydroxide. We have also further characterised it by the formation of the hydroxy-nitrile (III), the hydroxy-acid (IV), the ethoxy-derivative (V), and the acid (VI) which is formed by condensing it with the sodium compound of ethyl malonate and hydrolysing the product. Experiments were also carried out in order



to ascertain whether the state of dilution of the potassium cyanide had any influence on the course of the reaction in the three series, but this was found not to be the case, and it is evident, therefore, that the property of asymmetric replacement in a compound possessing apparent symmetry is characteristic of the meta-series.

## EXPERIMENTAL.

*The Interaction of Alcoholic Potassium Cyanide (1 mol.) and  $\omega\omega'$ -Dibromo-o-(and p-)xylene (1 mol.).*

*$\omega\omega'$ -Dibromo-o-xylene.*—This operation was carried out in a manner similar to that described in the earlier paper (Moore and Thorpe, T., 1908, **93**, 175), but care was taken to keep, as far as possible, to the theoretical amounts required by equation (1) (p. 1156).

Fifty-three grams of pure  $\omega\omega'$ -dibromo-o-xylene melting at  $95^{\circ}$ , and in a finely ground condition, were added gradually to a boiling solution containing 13 grams of Kahlbaum's purest potassium cyanide, which had been prepared by dissolving the cyanide in the smallest possible amount of cold water and adding three times the volume of absolute alcohol. When all the dibromide had been added, the mixture was allowed to remain for half an hour, when it was diluted with water, and the oil, which was then precipitated, extracted with ether. The dried ethereal solution was freed from the solvent, and the oily residue submitted to careful fractionation under diminished pressure (20 mm.). The fraction boiling below  $160^{\circ}$  was then redistilled, and the portion boiling between  $135^{\circ}$  and  $140^{\circ}$  collected. The distillate solidified, and was found to melt, without further purification, at  $94-95^{\circ}$ . An analysis (Found: Br=60.71.  $C_8H_8Br_2$  requires Br=60.6 per cent.) proved it to be pure  $\omega\omega'$ -dibromo-o-xylene. The amount recovered weighed 24.7 grams, or, in other words, it represented approximately 50 per cent. of the dibromo-compound originally used.

*$\omega\omega'$ -Dibromo-p-xylene.*—In this case, the same conditions and quantities as those given above were used, excepting that, after all the dibromide had been added, the mixture was heated on the water-bath for four hours. Fractionation of the oily product gave a quantity of distillate boiling below  $160^{\circ}/20$  mm., and this on redistillation gave 25 grams of liquid boiling at  $145^{\circ}/21$  mm., which rapidly solidified in the receiver. The solid melted, without further purification, at  $143^{\circ}$ , and an analysis (Found: Br=60.56.  $C_8H_8Br_2$  requires Br=60.6 per cent.) proved it to be pure  $\omega\omega'$ -dibromo-p-xylene. In this case also it is evident that the reaction had proceeded in accordance with equation (1) (p. 1156), and that approximately 50 per cent. of the dibromo-compound had been recovered unchanged.

The residue left in the flask after the  $\omega\omega'$ -dibromo-o-xylene had been distilled off, together with a small quantity obtained on subsequently refractionating the distillate, solidified on cooling, and

when recrystallised from alcohol yielded 14.5 grams of pure  $\sigma$ -phenylenediacetonitrile melting at  $60^{\circ}$ . On the other hand, the residues from the  $\omega\omega'$ -dibromo-*p*-xylene experiment, which also solidified on cooling, gave only 8 grams of the dinitrile melting at  $98^{\circ}$  when recrystallised.

*The Interaction of  $\omega\omega'$ -Dibromo-*m*-xylene and Alcoholic Potassium Cyanide under Different Conditions.*

- (1) *Experiments involving the Use of  $\omega\omega'$ -Dibromo-*m*-xylene\* (1 mol.) and Potassium Cyanide (2 mols.). (a) Oddo's Method (loc. cit.).*

$\omega\omega'$ -Dibromo-*m*-xylene (13.4 grams) and 9 grams of potassium cyanide (pure and finely ground) were mixed with 500 c.c. of alcohol and heated in a flask fitted with a reflux condenser for twenty hours on the water-bath. The alcohol was then distilled off and water added, the precipitated oil and aqueous liquid being extracted by ether. The washed and dried ethereal solution yielded an oil on evaporating the solvent, which, when distilled under 18 mm. pressure, gave 9.5 grams of a colourless oil boiling at  $140$ — $141^{\circ}$ . This oil appeared to be the sole product of the reaction.

(b) The quantities and conditions employed in this case were based on those used by Atkinson and Thorpe (T., 1907, 91, 1699) for the production of the three tolylacetonitriles. Sixty grams of pure, finely ground potassium cyanide were dissolved in the smallest possible quantity of water, and then diluted to 500 c.c. with alcohol. To this solution were added 50 grams of recrystallised  $\omega\omega'$ -dibromo-*m*-xylene dissolved in 200 c.c. of alcohol. The whole was then heated on the water-bath under a reflux condenser for twenty-four hours, when it was noticed that, after the reaction had been in progress for two hours, an orange-coloured precipitate formed, the amount of which continued to increase for some time. At the end of the time specified, the alcohol was removed by distillation, water added in sufficient quantity to dissolve the potassium salts, and the mixture, after being cooled to  $0^{\circ}$ , filtered. The precipitate was then washed with hot alcohol, in which the nitrile is readily soluble, and the oil recovered from the alcohol in the usual way. It boiled at  $140$ — $141^{\circ}$ /18 mm., and weighed 36 grams; there was no fraction of higher boiling point. The orange-coloured precipitate was purified by repeated extraction with hot alcohol and then with boiling water. It was an amorphous substance evidently of high molecular weight, since it did not melt and was insoluble in all the

\* In all the experiments described in this section pure  $\omega\omega'$ -dibromo-*m*-xylene melting at  $76$ — $77^{\circ}$  was used.

usual organic solvents. An analysis showed it to contain N=10.4 per cent., but we have not as yet been able to assign any constitution to it. Its formation was evidently due to the large excess of potassium cyanide used in the reaction.

(c) Finally, an experiment was carried out in order to see whether the dilution of the potassium cyanide had any important influence on the nature of the product, the proportions used being the same as those given by Oddo. Thus, 53.6 grams of the dibromo-compound and 36 grams of potassium cyanide were taken, together with 500 c.c. of alcohol, that is, about one-fourth the quantity used by Oddo, the reaction being carried out in precisely the same way as described in experiment (a). Here again the sole product was a colourless oil boiling at 140—141°/18 mm., the weight obtained being 38 grams.

(2) *Experiment involving the Use of  $\omega'$ -Dibromo-m-xylene (1 mol.) and Potassium Cyanide (1 mol.).*—The conditions used in this experiment were the same as those given in the case of  $\omega'$ -dibromo-*o*-(and *p*-)xylene on p. 1159, the mixture being, however, heated for ten hours on the water-bath before being worked up. In this case, the whole of the liquid product boiled at 140—141°/18 mm., that is, at practically the same temperature as the dibromo-compound used. An analysis showed, however, that it was the pure bromo-nitrile (Found: Br=38.12.  $C_9H_8Br_2$  requires Br=60.6;  $C_9H_8NBr$  requires Br=38.1 per cent.). The yield was almost theoretical.

*$\omega$ -Bromo-m-tolylacetonitrile (I, p. 1158).*

This substance, prepared by any of the methods described above, is a colourless, mobile liquid which, as already stated, boils at 140—141°/18 mm., or, with slight decomposition, at 220—221°/756 mm. The yield is approximately 90 per cent. of that theoretically possible:

0.0863 gave 0.1625  $CO_2$  and 0.0313  $H_2O$ . C=51.45; H=4.05.

0.2099 (by Carius' method) gave 0.1879 AgBr. Br=38.10.

0.4865 (by alcoholic  $AgNO_3$ ) required 0.3698  $AgNO_3$ . Br=37.99.

$C_9H_8NBr$  requires C=51.4; H=3.8; Br=38.1 per cent.

An attempt to determine the nitrogen content failed, owing to the fact that the substance reacted with copper oxide at the ordinary temperature, and the combustion was therefore practically complete before the air had been swept from the tube. An estimation was carried out by Kjeldahl's method, but here again no accurate result was obtained, due doubtless to the destruction of part of the ammonia by the bromine liberated. The bromo-nitrile is in many

ways a curious compound, and is very inert towards most of the usual reagents. For example, it is not acted on by concentrated hydrochloric acid even after prolonged boiling, and is unaffected by 64 per cent. aqueous potassium hydroxide or by mild reducing agents. On the other hand, it gives a characteristic reaction with concentrated sulphuric acid, forming, even when only very small quantities are used, a deep reddish-brown solution which rapidly sets to a jelly. The action of water precipitates a yellow powder which, as the following analysis shows, possesses the same empirical formula as the original bromo-nitrile:

0.1563 gave 0.2940  $\text{CO}_2$  and 0.0549  $\text{H}_2\text{O}$ .  $\text{C}=51.3$ ;  $\text{H}=3.9$ .

0.2542 „ 0.2270  $\text{AgBr}$ .  $\text{Br}=38.0$ .

0.2136 „ 12 c.c.  $\text{N}_2$  at  $15^\circ$  and 765.8 mm.  $\text{N}=6.65$ .

$\text{C}_9\text{H}_8\text{NBr}$  requires  $\text{C}=51.4$ ;  $\text{H}=3.8$ ;  $\text{N}=6.7$ ;  $\text{Br}=38.1$  per cent.

The structure of this substance is under investigation.

*ωω'*-Dihydroxy-*m*-xylene (II, p. 1158) and *ω*-Hydroxy-*m*-tolyl-acetonitrile (III, p. 1158).

The bromo-nitrile is readily converted into a mixture of these two substances when it is treated for half an hour with an excess of freshly precipitated silver hydroxide. The oil, which can be extracted from the product, after filtration, by ether, can be readily separated into two fractions, one boiling at  $154\text{--}159^\circ/13$  mm., and another boiling at  $145^\circ$  under the same pressure. The former solidifies on keeping and melts at  $47^\circ$  (Found:  $\text{C}=69.6$ ;  $\text{H}=7.2$ .  $\text{C}_8\text{H}_{10}\text{O}_2$  requires  $\text{C}=69.5$ ;  $\text{H}=7.2$  per cent.). Since it readily gives isophthalic acid on oxidation, it is evidently *ωω'*-dihydroxy-*m*-xylene, originally prepared by Colson (*loc. cit.*). The fraction of lower boiling point ( $145^\circ/13$  mm.) was analysed:

0.1403 gave 0.3770  $\text{CO}_2$  and 0.0770  $\text{H}_2\text{O}$ .  $\text{C}=73.3$ ;  $\text{H}=6.1$ .

0.1346 „ 10.95 c.c.  $\text{N}_2$  at  $16^\circ$  and 762.3 mm.  $\text{N}=9.54$ .

$\text{C}_9\text{H}_9\text{ON}$  requires  $\text{C}=73.5$ ;  $\text{H}=6.1$ ;  $\text{N}=9.5$  per cent.

It is evidently *ω*-hydroxy-*m*-tolylacetonitrile, since it yields *ω*-hydroxy-*m*-tolylacetic acid (see below) on treatment with hydrochloric acid. The hydroxy-nitrile is a colourless, pleasant-smelling oil which decomposes when distilled under the ordinary pressure. Although their boiling points lie so close together, the separation of these two compounds by fractional distillation is complete.

*ω*-Hydroxy-*m*-tolylacetic Acid (IV, p. 1158).

This acid can be prepared from the above hydroxy-nitrile by boiling it with concentrated hydrochloric acid, and from the bromo-

nitrile by treatment with aqueous sulphuric acid (1:1) in a sealed tube for six hours at 150°. The acid is extracted by ether, and it is advisable to neutralise the residue, left after evaporating the ether, with dilute ammonia, and again to extract with ether, in order to remove non-acidic impurities, before finally precipitating the acid by means of hydrochloric acid. It crystallises from dilute hydrochloric acid in white, glistening plates melting at 128°:

0.1532 gave 0.3656 CO<sub>2</sub> and 0.0835 H<sub>2</sub>O. C=65.0; H=6.05.

C<sub>9</sub>H<sub>10</sub>O<sub>3</sub> requires C=65.1; H=6.0 per cent.

The acid is freely soluble in alcohol, ether, or hot water.

*ω*-Ethoxy-m-tolylacetonitrile (V, p. 1158).

The bromo-nitrile (10.5 grams) is converted into this ethoxy-derivative when it is treated with an alcoholic solution of sodium ethoxide—prepared by dissolving 1.2 grams of sodium in 30 c.c. of alcohol—in the first instance at the ordinary temperature for eight hours, and finally on the water-bath for one hour. Water is then added and the oil extracted by ether, the dried ethereal solution leaving a residue on evaporation which, on distillation, yields the ethoxy-derivative as a colourless, mobile oil boiling at 161–162°/13 mm.:

0.1020 gave 0.2790 CO<sub>2</sub> and 0.0712 H<sub>2</sub>O. C=74.59; H=7.6.

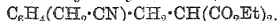
0.1285 „ 8.60 c.c. N<sub>2</sub> at 14° and 768.1 mm. N=7.99.

C<sub>11</sub>H<sub>13</sub>ON requires C=75.4; H=7.4; N=8.0 per cent.

It is a remarkable fact that although the above Dumas estimation gave results in accordance with theory, and that the odour of ammonia could be detected when the compound was hydrolysed by alkali, several very careful tests by the metallic sodium method failed to reveal a trace of nitrogen.

*The Condensation of Ethyl Sodiomalonate with ω-Bromo-m-tolyl-acetonitrile.*

*Ethyl ω-Cyano-m-methylbenzylmalonate,*



—This substance is formed by allowing a solution containing 16 grams of ethyl malonate, which has been converted into its sodium derivative by means of 1.2 grams of sodium dissolved in 30 grams of alcohol, to react with 10.5 grams of the bromo-nitrile at the temperature of the water-bath for four to five hours. It is precipitated as an oil on the addition of water, and can be extracted with ether and isolated in the usual way. The ester boils at 201–203°/18 mm.:



0.1266 gave 0.3082  $\text{CO}_2$  and 0.0754  $\text{H}_2\text{O}$ .  $\text{C}=66.39$ ;  $\text{H}=6.62$ .

0.3012 „ 12.9 c.c.  $\text{N}_2$  at  $17^\circ$  and 764.4 mm.  $\text{N}=4.9$ .

$\text{C}_{16}\text{H}_{19}\text{O}_4\text{N}$  requires  $\text{C}=66.4$ ;  $\text{H}=6.6$ ;  $\text{N}=4.8$  per cent.

The ester is quickly hydrolysed, by a solution containing rather more than the calculated quantity of sodium hydroxide, at a gentle heat, and the acid,  $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{CN})\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})_2$ , is formed as a crystalline precipitate when the solution is acidified. It was not found possible, however, to recrystallise this acid, because when its solutions in solvents are heated, carbon dioxide is quickly eliminated. If, for example, its aqueous solution is boiled,  *$\beta$ -w-cyano-m-tolylpropionic acid*,  $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{CN})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , separates on cooling. This acid crystallises from water, containing a little hydrochloric acid, in white, glistening plates melting at  $148^\circ$ , and closely resembling anthracene in appearance:

0.1124 gave 0.2878  $\text{CO}_2$  and 0.0590  $\text{H}_2\text{O}$ .  $\text{C}=69.79$ ;  $\text{H}=5.90$ .

0.1758 „ 11.5 c.c.  $\text{N}_2$  at  $20^\circ$  and 757.9 mm.  $\text{N}=7.41$ .

$\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}$  requires  $\text{C}=69.8$ ;  $\text{H}=5.8$ ;  $\text{N}=7.4$  per cent.

*$\beta$ -w-Carboxy-m-tolylpropionic Acid* (VI, p. 1158).

This acid is best prepared from the cyano-acid described above by dissolving it in three times its weight of concentrated sulphuric acid, allowing the solution to remain for two hours, and then, after diluting it with three times its volume of water, boiling for three hours. The acid is then collected and washed with ether, being finally recrystallised from dilute alcohol, when it is obtained in fine needles which melt at  $132^\circ$ :

0.1045 gave 0.2431  $\text{CO}_2$  and 0.0543  $\text{H}_2\text{O}$ .  $\text{C}=63.40$ ;  $\text{H}=5.82$ .

$\text{C}_{11}\text{H}_{12}\text{O}_4$  requires  $\text{C}=63.5$ ;  $\text{H}=5.8$  per cent.

The acid is sparingly soluble in hot water or ether, but readily so in alcohol. The *calcium* salt is insoluble in hot water, and the *potassium* salt crystallises from water in plates.

This work was carried out during the tenure by one of us (W.H.G.) of a fellowship granted by the Salters' Company.

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SOUTH KENSINGTON. [Received, September 3rd, 1919.]

#### CIV.—*Molecular-weight Determination by Direct Measurement of the Lowering of the Vapour Pressure of Solutions.*

By ROBERT WRIGHT.

THE direct measurement of the vapour pressure of solutions has never been very extensively used as a means of determining molecular weights. The barometric method as originally employed by Raoult is too cumbersome for general use, and at the ordinary temperature the lowerings of the vapour pressure obtained with most solvents are too small to admit of accurate measurement by this means. A simple method for use with a volatile liquid, such as ether, was described in a former paper (P., 1912, 28, 96), but it is quite unsuitable in the case of the more common solvents.

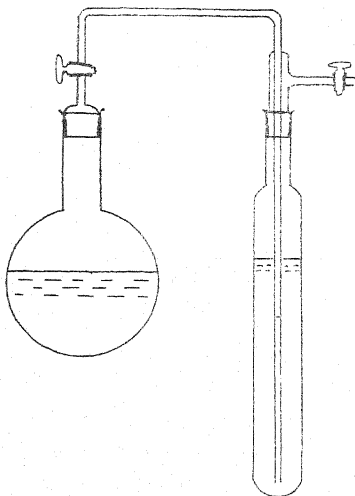
Menzies (*J. Amer. Chem. Soc.*, 1910, 32, 1615) has described an apparatus in which the lowering of the vapour pressure produced by a solute is measured at the boiling point of the solution, the manometric liquid used being the solution itself; so that, both on account of the high temperature of the determination and the sensitiveness of the manometer, very dilute solutions can be employed in the measurements.

The apparatus about to be described resembles that of Menzies in that the solution is used as the manometric liquid, but all measurements are carried out at the ordinary temperature, and as the apparatus is of simple design, it can readily be constructed of ordinary laboratory material. A flask, or bottle, of 150 c.c. capacity is fitted with a ground-in delivery tube which carries a well-fitting tap placed just above the flask, the other end of the delivery tube passing almost to the bottom of a test-tube about 20 cm. long and 2—3 cm. wide. The neck of the test-tube is fitted with a hollow stopper, through which the delivery tube is sealed; the stopper also carries a side-tube fitted with a tap. It will be seen that the test-tube is of the same construction as an ordinary Drechsel gas-washing bottle fitted with a stop-cock; in fact, the first piece of apparatus employed consisted of such a wash-bottle; it was, however, abandoned, on account of the large amount of solution required, and the smaller test-tube substituted.

In carrying out a determination, a weighed quantity of the solute is placed in the test-tube, and after both flask and tube have been half filled with solvent, the apparatus is connected together,

all ground connexions being carefully treated with rubber grease. The apparatus is now exhausted by means of a filter-pump so that all air is boiled out of both solvent and solution; to assist this boiling-out process, the flask containing the solvent may be heated gently, either with the hand or by means of a beaker of warm water; it is also advisable to sweep out the air in gusts by alternately closing and opening the tap between the flask and test-tube.

When exhaustion is complete, a process which should occupy



about half an hour, both taps are closed and the apparatus is left to itself for two or three hours to attain the ordinary temperature. The tap between the flask and test-tube should be closed during this period to prevent the forcing back of the solution into the pure solvent as a result of accidental leakage of air into the test-tube. When the ordinary temperature has been reached, the tap above the flask is gently opened, and as the vapour pressure of the solvent exceeds that of the solution, the liquid in the delivery tube is depressed below the ordinary level of the liquid in the test-tube.

This difference in height is measured either by means of a cathetometer or by having the delivery tube graduated in mm.; in either case, the observed height must be corrected for capillarity. As a check on the manometer reading, it is usually advisable to re-exhaust the apparatus without warming the solvent flask, and as the solution in the test-tube will remain practically unchanged in volume, a second pressure-reading almost identical with the first should be obtained. The temperature of the room is noted at the same time as the manometer reading is taken, and air is then admitted to the apparatus by gently raising the tap above the flask out of its seat, care being taken to prevent a violent inrush of air; the effect of capillarity is now noted, after which the test-tube is removed and weighed, and the mass of the solution so determined. If the solution is a concentrated one, its density should also be measured; in the case of dilute solutions, the density may be considered as equal to that of the solvent.

The molecular weight of the solute is calculated from the usual formula for the lowering of the vapour pressure,

$$M = \frac{P'Sm}{(P - P')s}$$

where  $M$  and  $m$  are the molecular weights of the solute and solvent,  $S$  and  $s$  their weights in grams,  $P$  the vapour pressure of the pure solvent, and  $P'$  that of the solution. The vapour pressure of the pure solvent at the temperature of the experiment is obtained by consulting tables, interpolating, if necessary, on the assumption that the curve connecting the logarithm of the vapour pressure and the temperature is a straight line.

The results obtained with alcohol and carbon tetrachloride as solvents are shown in the following table:

*Alcohol as Solvent.*

Solute	$S$ .	$s$ .	$T$ .	$P$ .	$H$ .	$P - P'$ .	$M$ .	$M(\text{true})$
Benzoic acid .....	5.698	78	19.5	42.6	17.8	1.084	128	122
Carbamide .....	4.043	108	19.0	41.4	21.0	1.237	56	60
Acetamide .....	3.781	102	17.0	36.6	17.5	1.039	59	59

*Carbon Tetrachloride as Solvent.*

Naphthalene .....	0.784	48	15.5	73.3	13.0	1.517	118	128
Phenanthrene ...	1.072	49	19.0	87.1	14.6	1.697	168	178

The headings of the different columns have the meanings ascribed to them in the formula. Column  $H$  gives the manometer readings in mm. of the solution, the heights being corrected for capillarity.

With regard to the solvents that may be employed, water is not

suitable, both on account of its very small vapour pressure and its low molecular weight. Alcohol and carbon tetrachloride were both satisfactory, although the latter showed some tendency to dissolve the rubber grease with which the taps were coated. The solvent action of the vapour on the tap lubricant quite prevented the use of benzene, and the plan of treating the taps with syrupy phosphoric acid instead of rubber proved unsuccessful, as the taps so lubricated seemed incapable of holding a vacuum.

A point of theoretical interest might be mentioned, as it applies both to the above method and that of Menzies. The vapour in the flask and delivery tube is confined between the pure solvent in the flask and the solution in the tube, and therefore it might be concluded that its pressure would lie between the values  $P$  and  $P'$ . Further consideration will show, however, that such a state is not in equilibrium, and that distillation will take place from the high pressure to the low, that is, from the solvent to the solution, until a layer of pure solvent is obtained lying on the top of the solution in the delivery tube, under which conditions the pressure of the vapour in the flask and delivery tube will be equal to that of the pure solvent.

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CV.—*The Constitution of Carbamides. Part X.  
The Behaviour of Urea and of Thiourea towards  
Diazomethane and Diazoethane respectively.  
The Oxidation of Thiourea by Potassium Per-  
manganate.*

By EMIL ALPHONSE WERNER.

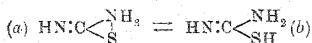
It was shown by Degner and von Pechmann (*Ber.*, 1897, **30**, 647) that urea is indifferent towards diazomethane dissolved in ether. In a recent communication (this vol., p. 1098), the author has drawn attention to the fact that the action of diazomethane as a methylating agent can be conveniently studied in alcoholic solution. It was considered desirable, therefore, to test the behaviour of urea under this condition, since the result of Degner and von Pechmann's experiment could not be reasonably accepted as final, on account of the insolubility of urea in ether.

It is now shown that even when diazomethane was generated in situ with urea dissolved in alcohol, which had been previously dried by means of diazomethane, the whole of the urea was recovered unchanged after it had remained for twenty-four hours in contact with the reagent. A similar result was obtained with diazoethane. This fact is in perfect agreement with the view that the cyclic form of the urea molecule alone obtains in a neutral solution. The reactive "amino-hydroxyl" configuration occurs only when a sufficiently strong acid or alkali is present, that is, under such conditions that a salt of the type  $\text{HN:C(OH)·NH}_2\text{·HX}$  or

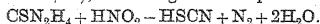


as the case may be, can exist in solution (T., 1918, 113, 86).

The case of thiourea is different. Its behaviour towards iodine, with the formation of formamidine disulphide (T., 1912, 101, 2175), the well-known reaction with alkyl haloids, whereby thioesters of the type  $\text{HN:C(SR)·NH}_2$  are produced, and particularly its reactions with nitrous acid (T., 1912, 101, 2180; 1913, 103, 1221), all go to prove that in a neutral solution thiourea must be present in two molecular forms in equilibrium, thus:

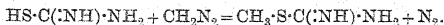


It may be well here to point out a fact which was not shown before (Expt. VI), namely, that, in contrast with urea (T., 1917, 111, 875), thiourea is rapidly decomposed by nitrous acid alone (at concentration  $N/30$ ), according to the equation



It is obvious that it is form (b) that is attacked by way of the amino-group, since the sulphur remains in its original state of combination in the decomposition product, namely, thiocyanic acid.

Convincing evidence in support of the above view is supplied by the fact that thiourea is attacked by diazomethane in alcoholic solution, thus:



The so-called methylisothiurea\* was readily isolated in the form of its picrate, which melted at  $221^\circ$ . The reaction proceeded slowly at first, indicating the presence of form (b) in small amount; as the temperature gradually rose, the velocity of the change from (a) to (b) was rapidly promoted. Since the free base is unstable,

\* The term "isothiurea" is commonly used with reference to its relation to the "thiocarbamide" formula, the existence of which the author does not admit under any conditions. Thiourea is "isothiurea" in its reactive form in solution.

it was partly decomposed, with the production of methyl mercaptan, the odour of which was evident as soon as the reaction commenced.

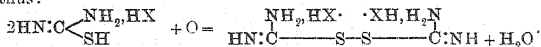
Ethylisothiurea picrate, which melted at  $188^{\circ}$ , was isolated from the reaction product when diazoethane was used, the change having proceeded on lines similar to the above.

When thiourea was treated with two molecular proportions of diazomethane, the excess of the latter showed no tendency to attack the methylisothiurea formed in the first instance, a result which, taken into consideration with the indifference of urea towards diazomethane, shows that an imino-group in the form  $\text{HN}:\text{C}:$  is not methylated by the reagent. In this connexion, it is interesting to note that the system  $\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot$  is capable of methylation; thus Pechmann (*Ber.*, 1895, 28, 855) obtained methylphthalimide, and Nierenstein (*private communication*) methylsuccinimide, from their respective parent compounds.

#### *Oxidation of Thiourea by Potassium Permanganate.*

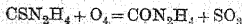
Interesting evidence in support of the existence of the two forms of thiourea in solution is supplied by a study of its oxidation by potassium permanganate under different conditions.

It was shown (T., 1912 and 1913, *loc. cit.*) that, in the presence of a sufficiently strong acid, a salt of isothiurea (*b*) was alone presented for attack, and hence formamidine disulphide was produced, thus:



Since the change from (*a*) to (*b*) is likewise promoted by the presence of alkali, oxidation in the presence of the latter should proceed on similar lines. This was found to be the case, but as formamidine disulphide cannot exist in the free state, its chief product of decomposition, namely, cyanamide, was obtained. The yield was 65 per cent. of the theoretical, whilst a certain amount of cyanic acid (as  $\text{NaOCN}$ ) was also formed. The mechanism of this change has yet to be fully studied, but one of the chief points to be noted is that no urea was produced under either of the above conditions.

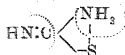
Maly (*Monatsh.*, 1890, 11, 277) has shown that urea is formed when thiourea is oxidised by potassium permanganate in a neutral solution, and whilst nearly all of the sulphur is oxidised to sulphuric acid, it was noted that the proportion of oxygen fell short of that required by the equation



which was given to represent the change.

A recent statement by Schmidt (*Arch. Pharm.*, 1918, 256, 308), in referring to Maly's experiment, that thiourea is quantitatively changed into urea by potassium permanganate, cannot be upheld.\* Maly distinctly stated that "the yield of urea was deceptive," and, as a matter of fact, only 5 grams of urea (theory=12 grams) were obtained from 15.2 grams of thiourea, and no explanation was given to account for the deficiency. A repetition of Maly's experiment gave a yield of urea equal to 44.4 per cent. of the theoretical, and whilst 98.7 per cent. of the sulphur was oxidised to sulphuric acid, the amount of potassium permanganate required to decompose the whole of the thiourea was approximately nine-tenths of the theoretical for four atoms of oxygen. Whilst ammonia and a small amount of carbon dioxide were formed as by-products, a crystalline substance having the composition  $C_3H_7N_5$  was isolated. This gave a silver derivative,  $C_3H_5N_3Ag_2$ , and the constitutional formula  $HN:C(NH_2) \cdot C(:NH) \cdot C(NH_2):NH$  is provisionally suggested to explain its formation.

Since urea could not be formed by the oxidation of *isothiurea* (form *b*), and as there was no evidence of the generation of cyanic acid during the reaction, the production of urea must, in all probability, have resulted from a direct replacement of sulphur by oxygen in the cyclic molecule (form *a*). It seems reasonable to expect that during the progress of such a change, since ammonia was one of the products, some thiourea would be decomposed, thus:



and from the union of  $HN:C:$  with two formamidine residues,  $HN:C \cdot NH_2$ , derived from the oxidation of *isothiurea* (*b*), the compound  $C_3H_7N_5$  would result.

The oxidation of thiourea in neutral solution is therefore in perfect agreement with the views put forward.

## EXPERIMENTAL.

### *Interaction of Thiourea and Diazomethane and Diazoethane Respectively.*

*Expt. I.*—1.52 Grams of thiourea and 2.1 grams of nitrosomethylurea were dissolved in 30 c.c. of alcohol which had been

\* A tendency to magnify unduly one change, to the exclusion of all others, has been very prevalent throughout the chemistry of urea, and, in the author's opinion, has been responsible for many of the erroneous conclusions which have been made.



previously dried \* by means of diazomethane. A solution of sodium ethoxide, prepared from 0.46 gram of sodium in 20 c.c. of alcohol, was added. There was at first a feeble evolution of nitrogen, which gradually became quite vigorous as heat was developed, and after about twenty minutes the golden-yellow colour of the solution had completely disappeared.

The solution, freed from the sodium cyanate which had been precipitated (see this vol., p. 1099), was added to 30 c.c. of a cold saturated aqueous solution of picric acid, the alcohol was removed by evaporation, and the sparingly soluble picrate which had separated on cooling was collected and purified by recrystallisation from hot water. It melted at  $221^{\circ}$ , which was also the melting point of the picrate prepared from the product of the action of methyl iodide on thiourea.

*Expt. II.*—This was similar to the above, but 4.2 grams of nitroso-methylurea and 0.92 gram of sodium dissolved in alcohol were used (that is, 2 mols. of diazomethane generated). After the evolution of nitrogen had ceased, the residual liquid had a rich golden-yellow colour, and after twenty-four hours it was dealt with as described under Expt. I, no other picrate than that which melted at  $221^{\circ}$  being isolated from the product. Excess of diazomethane was therefore without action on methylisothiurea.

*Expt. III.*—1.52 Grams of thiourea and 2.35 grams of nitroso-ethylurea were treated as in Expt. I. Similar phenomena were observed, and a picrate was obtained which melted at  $188^{\circ}$ :

0.1897 gave 33.4 c.c.  $N_2$  at  $14^{\circ}$  and 761.5 mm.  $N=20.8$ .

$C_3H_5N_2S, C_6H_3O_7N$  requires  $N=21.08$  per cent.

A picrate prepared from the product of the interaction of ethyl bromide and thiourea melted at  $188^{\circ}$ .

Experiments with urea, carried out in a similar manner, gave negative results.

#### *Oxidation of Thiourea by Potassium Permanganate.*

*A. In Neutral Solution. Expt. IV.*—To 0.076 gram of thiourea dissolved in 25 c.c. of water, 0.421 gram of potassium permanganate dissolved in 60 c.c. of water was added. After the reaction had been completed in the cold, the product was heated to  $100^{\circ}$ . The filtrate and washings gave  $BaSO_4=0.23$  gram. Theory requires  $BaSO_4=0.233$  gram. Hence 98.7 per cent. of the sulphur was oxidised to  $SO_2$ .

\* A small quantity of a concentrated ethereal solution of diazomethane was added to pure alcohol until the solution retained a pale yellow colour after remaining for twenty-four hours.

*Expt. V.*—22.8 Grams of thiourea were dissolved in 400 c.c. of water, and a hot saturated solution of potassium permanganate was added (about 116 grams were required) until a slight excess of the reagent remained after the product had been heated to 100° for five minutes. The filtrate and washings from the precipitated manganese dioxide were evaporated to dryness at 100°, and the residue was extracted with hot alcohol. After concentration of the latter solution, 1.2 grams of crystals, which had separated in rosette-like conglomerates of slender, glistening prisms, were collected. They were purified from the accompanying urea by recrystallisation from hot alcohol:

0.1868 gave 0.22 CO<sub>2</sub> and 0.1088 H<sub>2</sub>O. C=32.11; H=6.47.

0.1216 „ 64.7 c.c. N<sub>2</sub> at 17° and 765.25 mm. N=62.28.

C<sub>3</sub>H<sub>7</sub>N<sub>5</sub> requires C=31.85; H=6.19; N=61.96 per cent.

The compound decomposed without melting at above 200°, ammonia being evolved. On addition of ammoniacal silver nitrate to the aqueous solution, a bulky, white precipitate was formed.

0.2 Gram dissolved in dilute nitric acid required 12.2 c.c. of N/10-KSCN. Ag=65.88.

C<sub>3</sub>H<sub>5</sub>N<sub>5</sub>Ag<sub>2</sub> requires Ag=66.05 per cent.

Eight grams of nearly pure urea were obtained from the mother liquor of the above compound, equal to 44.4 per cent. of the theoretical.

*B. In Alkaline Solution. Expt. VI.*—To 0.152 gram of thiourea dissolved in 25 c.c. of water, 3 c.c. of *N*-sodium hydroxide and 0.842 gram of potassium permanganate dissolved in 100 c.c. of water were added. The oxidation was completed in a few minutes, after which the product was filtered and the precipitated manganese dioxide washed free from all soluble matter. The cyanamide present in the filtrate required 26 c.c. of *N*/10-ammoniacal silver nitrate for precipitation. Cyanamide found=0.0546. Theory requires 0.084. Hence 65 per cent. of the theoretical amount of cyanamide was present. Sodium cyanate, the amount of which was not determined, was also present, but whether this was derived from the direct oxidation of thiourea or from cyanamide first formed has not yet been ascertained. No urea was detected in the solution.

*Interaction of Thiourea and Nitrous Acid at Concentration N/30.*

*Expt. VII.*—0.076 Gram of thiourea and 0.072 gram of sodium nitrite were dissolved in 29 c.c. of water in the nitrometer, and 1 c.c. of *N*-acetic acid was added. Evolution of nitrogen at a moderate rate commenced after a few seconds.

Vol. of  $N_2$  (after forty minutes) = 23.6 c.c. at  $17^\circ$  and 767 mm. = 21.99 c.c. at *N.T.P.* Theory requires  $N_2$  = 22.4 c.c.

Under similar conditions, urea gave no nitrogen even after remaining for three days (compare T., *loc. cit.*).

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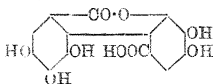
## CVI.—The Tannin of the Knopper Gall.

By MAXIMILIAN NIERENSTEIN.

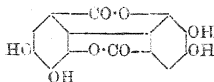
THE "Knopper Galls" (compare E. T. Connold, "Plant Galls of Great Britain," 1909, 254) or "Knoppfern," as they are known in the tanning industry (compare H. R. Procter, "The Principles of Leather Manufacture," 1903, 262), are the galls produced by *Cynips calicis*, Burgsdorff, on the immature acorns of various species of oaks, principally *Quercus cerris* of the Slavonic plains, where these galls are known locally by their Slavonic and Hungarian names, "Šisarca" and "gubacs" respectively.\* Their occurrence in Great Britain on *Quercus pedunculata* and also *Quercus sessiliflora* has been recorded by E. T. Connold ("British Oak Galls," 1908, 143), who refers to them also as "Gall-nuts." Löwe (*Zeitsch. anal. Chem.*, 1875, 13, 46), who has carried out the only published investigation on knoppfern tannin, described it as being identical with gallotannin. This, however, is not the case, as will be seen from the present communication. It is found that knoppfern tannin yields on hydrolysis, in addition to dextrose, not gallic acid, as is the case with gallotannin, but mainly ellagic acid (II) in common with other "bloom" (ellagic acid) producing

\* I am indebted for some of this information to Dr. Jan Jedlička, whom I have also to thank for the knoppfern used in this investigation. Dr. Jedlička drew my attention to the ease with which the knoppfern extracts deposited ellagic acid which he thought was due to the presence of a ferment in these galls, since he had succeeded in preventing the formation of ellagic acid by prolonged boiling of the extracts. I have attempted to isolate this ferment, but without success. In this connexion I may mention that I also found that emulsin has no effect on knoppfern tannin, which is of interest since this ferment readily hydrolyses the tannin of *Terminalia chebula* into dextrose, luteic acid, and ellagic acid (*Ber.*, 1910, 43, 1268). On the other hand, I found that *Penicillium* produces ellagic acid from knoppfern tannin which corresponds with the formation of gallic acid from gallotannin by *Penicillium* (compare Knudsen, *J. Biol. Chem.*, 1912, 14, 159; Asai, *J. Coll. Sci. Tokyo*, 1918, 39, 23).

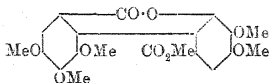
tannins (compare A. G. Perkin and Nierenstein, T., 1905, 87, 1412). It is also observed that methylated knopperrn tannin yields on hydrolysis a mixture of partly methylated luteoic acids (I), which give on further methylation with diazomethane methyl pentamethoxyluteoate (III). The latter substance was found to be



(I.)



(II.)



(III.)

identical with the lactone of methyl 2-hydroxy-3:4:4':5':6'-penta-methoxydiphenyl-6:2'-dicarboxylate (III), previously described by Herzig and Polack (*Monatsh.*, 1908, 29, 263). From these observations it is provisionally concluded that the knopperrn tannin molecule is composed of luteoic acid (I) and dextrose, the luteoic acid being predominant. Luteoic acid, which is an oxidation product of gallotannin (*Ber.*, 1908, 41, 3015), has also been found to be the predominant component of the tannin of *Terminalia chebula* (*Ber.*, 1910, 43, 1267). Reference ought also to be made to the presence of galloyl-*l*-leucine in the fat extracted from the knopper gall (*Zeitsch. physiol. Chem.*, 1914, 92, 53), and the production of ellagic acid from galloylglycine by *Penicillium* (*Biochem. J.*, 1915, 9, 240), which observations, in conjunction with the suggested configuration of knopperrn tannin, may be regarded as further evidence in support of the assumption made (*Biochem. J.*, 1915, 9, 241) that some nitrogenous galloyl derivatives serve as foodstuffs for the growing, gall-producing parasites and at the same time lead to the formation of "pathological" tannins, such as gallo-tannin, knopperrn tannin, and the other tannins found in galls (compare Nierenstein, *Ber.*, 1910, 43, 628; Drabble and Nierenstein, *Biochem. J.*, 1907, 2, 96; Nierenstein and Webster, *Ber.*, 1908, 41, 80).

#### EXPERIMENTAL.

##### *Preparation of Knopperrn Tannin.*

The powdered and finely sieved knopperrn were at first extracted with boiling chloroform or *s*-tetrachloroethane, so as to remove the

so-called gall-fats.\* The carefully dried powder was subsequently extracted with boiling acetone. In both cases the extraction was carried out in the extraction apparatus described elsewhere (Abderhalden, "Handbuch der biochemischen Arbeitsmethoden," 1912, 6, 149). The acetone extract was made up to 1.5 litres and the tannin precipitated with 300 c.c. of light petroleum which had been dried over calcium chloride. The crude tannin obtained in this way was purified by dissolving 50 grams of it in 1 litre of acetone and precipitating with four successive quantities of light petroleum of 100 c.c. each. It is necessary to dry both the acetone and the light petroleum over calcium chloride for some time, as otherwise the products obtained are viscid (compare also Manning and Nierenstein, this vol., p. 666). The fractions obtained weighed 26, 12, 6, and 2.5 grams respectively and were pale-coloured, amorphous products which neither melted nor decomposed when heated above 300°. They were soluble in alcohol, acetone, ethyl acetate, acetic acid, or water, but insoluble in benzene, light petroleum, or chloroform. The different solutions gave greenish-blue colorations with ferric chloride, which were particularly well-marked when the alcoholic solution was employed. This is of special interest in view of the generally accepted classification of the tannins into catechol and pyrogallol groups, which classification is based on the green and blue colorations given by these two groups respectively with ferric chloride. In this connexion it ought to be mentioned that the tannins of *Terminalia chebula* (Nierenstein, *loc. cit.*) and *Polygonum bistorta* (Stenhouse, *Phil. Mag.*, 1843, [iii], 23, 335; Eissfeld, *Annalen*, 1854, 92, 109; 1859, 111, 217; Bjalobreshesky, *Pharm. J.*, 1900, 22, 3; Iljin, *Diss.*, Petrograd, 1905, p. 38) show similar mixed colorations with ferric chloride. The aqueous solution of knoppern tannin precipitates alkaloids and gelatin, and is quantitatively adsorbed by caseinogen (compare Manning and Nierenstein, this vol., p. 667). Knoppern tannin is hygroscopic, and the determination of its elementary composition by combustion requires the same precautions as used by Geake and Nierenstein (*Ber.*, 1914, 47, 897) in the analysis of gallotannin.

Found:

Fraction I.—C=54.3; H=2.1. M.W. (in acetone)=1628, 1654, 1708. M.W. (in alcohol)=1744, 1682, 1664.

\* Preliminary investigations of the gall-fats of the knoppern seem to indicate that they are identical with the fats derived from Aleppo galls (compare Kunz-Krause and his collaborators, *Apoth. Zeit.*, 1897, 37, 734; *Arch. Pharm.*, 1904, 237, 256; 1907, 245, 28). These observations refer mainly to *cyclogallipharic* acid of the knoppern gall-fat, which had been obtained by Kunz-Krause's method. It crystallised, like his *cyclogallipharic* acid, from light petroleum in large scales melting at 88–89°.

Fraction II.— $C=54.1$ ;  $H=2.2$ .

Fraction III.— $C=55.4$ ;  $H=2.4$ . M.W. (in acetone)=1758, 1744, 1694. M.W. (in alcohol)=1742, 1716, 1758, 1708.

Fraction IV.— $C=55.6$ ;  $H=2.5$ . M.W. (in acetone)=1702, 1744, 1726. M.W. (in alcohol)=1758, 1744, 1726.

For the polariscopical investigations of knopperrn tannin only 0.5 per cent. solutions were used in view of the experiences of Navassarat (*Kolloid Zeitsch.*, 1913, **12**, 97) in the case of gallo-tannin:

Fraction I.— $[\alpha]_D^{25} + 31.8^\circ$  (in alcohol);  $+ 8.4^\circ$  (in acetone).

Fraction IV.— $[\alpha]_D^{25} + 36.2^\circ$  (in alcohol);  $+ 11.8^\circ$  (in acetone);  $+ 28.6^\circ$  (in water).

### *Hydrolysis of Knopperrn Tannin.*

About 0.5 gram of knopperrn tannin (Fractions III and IV only were used) was dissolved in 200 c.c. of water and heated with 20 c.c. of a 5 per cent. solution of sulphuric acid for eight to twelve hours on a water-bath, a reflux condenser being used. The ellagic acid formed was collected in a Gooch crucible and washed at first with cold water, so as to remove all traces of sulphuric acid, and afterwards with alcohol and ether. The precipitate was dried at  $130^\circ$  and weighed as ellagic acid. (Found,  $C=56.4$ ,  $55.8$ ;  $H=2.1$ ,  $2.2$ . Calc.,  $C=55.6$ ;  $H=2.0$  per cent.) The filtrate was tested for dextrose by Fischer and Freudenberg's method (*Ber.*, 1912, **45**, 915) and the dextrose was estimated volumetrically by Bertrand's method (*Bull. Soc. chim.*, 1906, [iii], **35**, 1286) as used by Nierenstein and Geake (*loc. cit.*) for the estimation of dextrose in gallo-tannin. In addition to this, the dextrose was also estimated polariscopically, in one case after the hydrolysis of 12.8 grams of knopperrn tannin. The dextrosazone was also prepared and found to have the correct melting point. (Found,  $N=15.9$ . Calc.,  $N=15.6$  per cent.)

Found: Ellagic acid= $84.6$ ,  $72.4$ ,  $81.2$ ,  $78.4$ . Dextrose= $7.2$ ,  $6.4$ ,  $5.8$ ,  $6.7$  (by Bertrand's method),  $7.8$  (polariscopically) per cent.

### *Methylated Knopperrn Tannin.*

The methylation (Fractions III and IV only were used) was carried out with diazomethane in ethereal suspension, and the same precautions were taken as in the case of hemlock tannin (compare Manning and Nierenstein, *loc. cit.*). The methylated knopperrn tannin dissolved completely in the ether and was purified several

times by dissolving it in alcohol and precipitating with water. The methylated knopperrn tannin obtained in this way was a colourless, amorphous product without any definite melting point. It was soluble in alcohol, acetone, chloroform, or *s*-tetrachloroethane, but insoluble in water or light petroleum.

Found: C=58.8, 57.9, 58.2; H=4.1, 4.4, 4.3; OMe=36.9, 37.4, 37.2, 37.8. M.W. (in alcohol)=1822, 1848, 1912. M.W. (in acetone)=1894, 1826, 1858.

The methoxyl estimations were carried out in a Zeisel-Perkin apparatus, acetic anhydride being added. If the latter was replaced by phenol (compare Weishut, *Monatsh.*, 1913, **33**, 1165) the same result (OMe=36.5) was obtained.

For the polariscopical investigations only 0.5 per cent. solutions were used, and the results obtained were as follows:

Found:  $[\alpha]_D^{18} + 4.2^\circ$  (in alcohol);  $+ 6.8^\circ$  (in acetone);  $+ 16.2^\circ$  (in chloroform);  $+ 28.2^\circ$  (in *s*-tetrachloroethane).

#### *Alkali Hydrolysis of Methylated Knopperrn Tannin.*

Methylated knopperrn tannin (about 5–10 grams) was hydrolysed by boiling with a 10 per cent. solution of alcoholic potassium hydroxide for eight hours, a reflux condenser being used. The alcohol was then evaporated and the residue extracted with boiling water, the extract being filtered from any unchanged or tarry material. On acidifying the cold solution with dilute sulphuric acid, there was obtained a bulky, colourless precipitate (Precipitate A), which was collected, washed, and dried in a desiccator. The filtrate was extracted several times with ether, which left on evaporation a tarry residue. Several attempts were made to isolate a definite disintegration product from this residue, but without success. The average yield of this residue corresponded with about 22 per cent. of the material hydrolysed. It did not reduce Fehling's solution.

*Precipitate A.*—This product proved to be a mixture, and it was found possible to separate it into two parts, respectively soluble and insoluble in benzene. The carefully dried substance was extracted in a Soxhlet apparatus with benzene, until a few drops of the overflow left no residue on evaporation. Five grams of the precipitate left about 2 grams in the thimble (Fraction I). The benzene solution gave on evaporation a second product (Fraction II). Both fractions were investigated separately.

*Fraction I.*—This product had no definite melting point (67–84°), and it was found impossible to crystallise it. The investigation of this amorphous material disclosed the following interest-

ing points, which might, perhaps, in time, prove of importance in the chemistry of knopperr tannin. It was found that the alcoholic solution gave a pronounced green coloration with ferric chloride, thus indicating (1) that it contained two hydroxyl groups in the ortho-position, and (2) that these two hydroxyl groups escaped methylation during the action of diazomethane on knopperr tannin. Attempts were also made to oxidise the alcoholic solution with silver oxide (Willstätter and Pfannenstiel, *Ber.*, 1904, 37, 4744) or *p*-benzoquinone (A. G. Perkin, T., 1913, 103, 661; Nierenstein, T., 1915, 107, 860) in the hope of obtaining the corresponding *o*-quinone. These experiments, however, only gave negative results.

Found: C=56.8, 57.1; H=4.4, 4.2; OMe=27.8, 26.4, 27.3.

These analytical data indicated that Fraction I was still a mixture consisting of tetramethoxyluteoic acid (Calc., C=57.4; H=4.2; OMe=32.9 per cent.) and trimethoxyluteoic acid (Calc., C=56.3; H=3.8; OMe=25.6 per cent.), the latter being predominant.

That Fraction I was a mixture was also proved on acetylation with acetyl chloride and pyridine. The acetyl derivative was also amorphous, and decomposed on heating at about 129—135°. Only acetyl estimations by A. G. Perkin's method (T., 1905, 87, 107) were made, which gave Ac=14.5, 13.8, 14.2 per cent., whereas the mono- and the di-acetyl derivatives require Ac=10.2 and 19.3 per cent. respectively.

On further methylation with diazomethane in ethereal solution Fraction I was entirely converted into methyl pentamethoxyluteoate (III), which crystallised from alcohol in small needles melting at 110°; this is in the vicinity of the melting point, 109—111°, given by Herzig and Polack (*loc. cit.*) for this substance. For comparison, the acid was also prepared by the method described by these authors from ellagic acid, when it was also found to melt at 110°. There was no depression of the melting point when the two preparations were mixed. (Found, C=59.1; H=5.1; OMe=46.3.  $C_{26}H_{20}O_9$  requires C=59.4; H=4.9; OMe=46.1 per cent.)

*Fraction II.*—This fraction did not give clearly the colour reaction with ferric chloride mentioned above, but the analytical data obtained for it agreed on the whole better for tetramethoxyluteoic acid than for trimethoxyluteoic acid, although in view of the amorphous character of the product and its indefinite melting point, which was found to be 98—112°, it seems obvious that the material was not pure. (Found, C=57.8, 57.6; H=4.5, 4.7; OMe=31.7, 31.4, 31.6.  $C_{13}H_{16}O_9$  requires C=57.4; H=4.2; OMe=32.9 per cent.)



It was found possible to acetylate Fraction II with acetyl chloride and pyridine, but a satisfactory product was not obtained. (Found, Ac=11.8, 12.2, 12.0. Calc., Ac=10.2 per cent.)

On further methylation with diazomethane, Fraction II was entirely converted into methyl pentamethoxyluteate (III); small needles melting at 110° were obtained, and this melting point was not changed by admixture with Herzig and Polack's product. (Found, C=59.2; H=4.9; OMe=46.1. Calc., C=59.4; H=4.9; OMe=46.1 per cent.)

This investigation has, with many interruptions, been in progress since 1907, during which time the author has had the collaboration of Dr. D. Spence and Messrs. R. J. Thompson, J. F. Fielding, C. W. Spiers, and F. S. Wallis, for which he wishes to thank them. The author is also indebted to the Research Fund Committee of the Chemical Society and the Colston Society of the University of Bristol for grants in aid of this investigation.

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## CVII.—*The Oxidation of Phenol Derivatives.*

By CYRIL NORMAN HINSHELWOOD.

THE observation that phenol in aqueous solution is completely and instantly oxidised by potassium permanganate whilst picric acid is very much more stable led to the examination of a number of other phenol derivatives. The mononitrophenols and the hydroxybenzoic acids are, like phenol itself, attacked by *N*/10-potassium permanganate with great rapidity. Bradshaw (*Amer. Chem. J.*, 1906, **35**, 326) carried out experiments from which he concluded that the order of attack at 0° was ortho, meta, para in acid solution and meta, ortho, para in alkaline solution. This is in accord with some older results of Dreyfus (*Compt. rend.*, 1887, **105**, 523).

Care must be exercised in drawing conclusions as to stability from the rate at which potassium permanganate is destroyed. The oxidation occurs in a series of stages of which only the first involves the breaking of the ring. Consequently, the initial rate of oxidation is the true measure of stability and the later stages are of minor importance. It is, of course, necessary to avoid complications due to the oxidation of side chains.

The method adopted for measuring the rate of oxidation was as follows. Aqueous solutions of the substances to be tested were prepared of such strength that for complete oxidation to carbon dioxide and water (and nitric acid in the case of nitro-compounds) an equal volume of  $N/10$ -potassium permanganate would be required. In making the calculation it was assumed that five atoms of oxygen would be yielded by the permanganate. Twenty-five c.c. of the solution were mixed with 50 c.c. of  $N/10$ -potassium permanganate and 10 c.c. of  $N/5$ -sulphuric acid in a thermostat adjusted to  $25.0^{\circ}$  and allowed to react for a measured time. The reaction was then stopped by the addition of potassium iodide and the liberated iodine titrated with  $N/10$ -sodium thiosulphate. As a matter of fact the potassium permanganate only yielded three atoms of oxygen, and brown oxide of manganese was always precipitated. As, however, double the amount was used which would be required if five atoms were given up, there was still an excess even when only three atoms were yielded. Moreover, the estimation of the iodine liberated gave results directly in terms of oxygen employed, independently of the actual state to which the manganese was reduced, so that complete oxidation still corresponded with a diminution of the thiosulphate titre of the mixture by 25 c.c. Two further points may be mentioned. Gooch has pointed out that acid solutions of potassium permanganate slowly lose oxygen. It was ascertained by blank determinations that no loss occurred in the longer experiments from this cause. Secondly, although the presence of any considerable amount of nitric acid is very undesirable in working with sodium thiosulphate, the concentration of that produced by the oxidation of the nitro-compounds was not sufficient to vitiate the results in any way. It was only necessary to ensure by efficient shaking that the thiosulphate did not remain in local excess during the titration.

Some results obtained with salicylic acid and with *p*-nitrophenol may be quoted first, as they serve to illustrate the complex course of the reaction and the condition for a good measure of stability.

The salicylic acid was recrystallised from water, and the *p*-nitrophenol was recrystallised twice from water and from hydrochloric acid. The pipettes and burettes were standardised, and the potassium permanganate and sodium thiosulphate solutions compared with each other daily.

The thermostat remained constant to about  $0.01^{\circ}$ .

## (1) Salicylic acid.

0.4929 gram per litre.

25 c.c. Salicylic acid solution

50 c.c.  $N/10\text{-KMnO}_4$ 10 c.c.  $N/5\text{-Sulphuric acid}$ 

Time in minutes.	Amount of oxygen used up in terms of c.c. $N/10\text{-Na}_2\text{S}_2\text{O}_3$
0.5	16.6
1.5	18.05
3.5	18.53
21	19.60
37	20.15
110	22.0
150	22.20
320	23.18
$\infty$ (theor.) for complete oxidation to carbon dioxide and water.	25.0

(2) *p*-Nitrophenol.

0.496 gram per litre.

25 c.c. *p*-Nitrophenol solution50 c.c.  $N/10\text{-KMnO}_4$ 10 c.c.  $N/5\text{-Sulphuric acid}$ 

Time in minutes.	Amount of oxygen used up in terms of c.c. $N/10\text{-Na}_2\text{S}_2\text{O}_3$
0.55	13.2
3.0	14.75
13.5	17.2
24.5	17.5
30	17.6
38	18.13
43	18.45
54.5	19.38
61.5	20.03
75.5	20.57
$\infty$ (theor.) for complete oxidation to carbon dioxide, nitric acid, and water.	25.0

It is clear that we have to deal in each case with consecutive reactions, the first stage of which is almost immeasurably rapid. Differences in the later stages will depend on the nature of the intermediate open-chain products, and throw no light on the stability of the original compound. This point does not seem to have received sufficient attention from Dreyfus and Bradshaw.

With the more highly substituted phenols quite trustworthy measurements can be made, and comparisons of stability obtained. Picric acid was taken as a standard of reference.

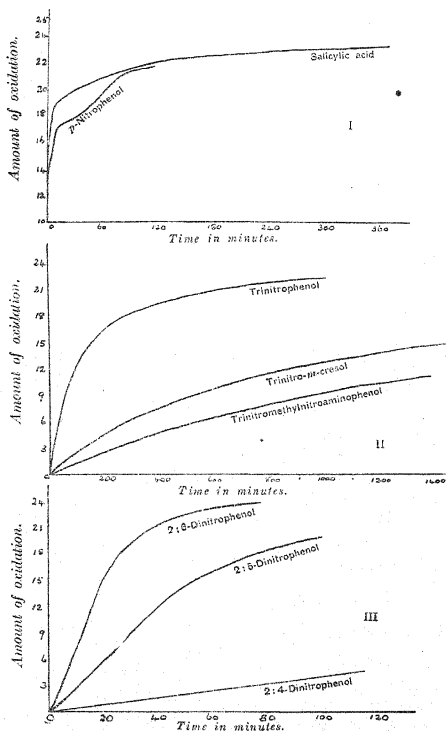
*Picric Acid*.—"Pure" picric acid was recrystallised twice from water. The solution contained 0.818 gram per litre.

(3) Picric acid 25 c.c.  
 $N/10\text{-KMnO}_4$  50 c.c.  
 $N/5\text{-Sulphuric acid}$  10 c.c.

Time in minutes.	Amount of oxygen used up in terms of c.c. $N/10\text{-Na}_2\text{S}_2\text{O}_3$ .	$k$ (see below).
$t$ .	$x$ .	
15	2.95	0.000130
28-25	4.68	0.000125
45	6.98]	0.000122
83	10.50	0.000119
120	12.98	0.000120
208	16.10	0.000110
255.8	17.12	0.000105
930	21.80	—
2340	23.0	—
$\infty$ (theor.)	25.0	—

Mean 0.000119

In calculating  $k$  it is assumed that the permanganate yields three atoms of oxygen, so that its concentration is initially proportional



to  $3/5 \times 50 = 30$ . The initial concentration of the picric acid is proportional to 25, and

$$k = \frac{1}{(30 - 25)t} \log_{10} \frac{5(30 - x)}{6(25 - x)};$$

$k$  being calculated for a reaction of the second order and its value

being fairly constant over the whole range, there is little evidence here of consecutive reactions. Evidently the first stage, namely, that involving the rupture of the ring, proceeds more slowly than the subsequent reactions. This accounts for the simple nature of the effect, and is confirmed by the fact that the later stages in the oxidation of *p*-nitrophenol and salicylic acid are more rapid than the corresponding stage of the picric acid reaction. *k* then is a measure of the stability of the picric acid molecule towards oxidation.

The effect of dilution was examined, so that less readily soluble substances might subsequently be compared with picric acid, using more dilute solutions. Incidentally, the results confirm the bimolecular nature of the change.

(4) Picric acid solution	25 c.c.
N/10-KMnO <sub>4</sub>	50 c.c.
N/5-Sulphuric acid	10 c.c.
	85 c.c.
+ water	85 c.c.

(5) Picric acid solution	25 c.c.
N/10-KMnO <sub>4</sub>	50 c.c.
N/5-Sulphuric acid	10 c.c.
	85 c.c.
+ water	170 c.c.

$k = \frac{2}{(30-25)t} \log_{10} \frac{5(30-x)}{6(25-x)}$		
<i>t.</i>	<i>x.</i>	
60	5.05	0.000120
156.5	9.65	0.000111
240	12.45	0.000111
305	13.87	0.000107
435	15.97	0.000103

Mean 0.000110

$k = \frac{3}{(30-25)t} \log_{10} \frac{5(30-x)}{6(25-x)}$		
<i>t.</i>	<i>x.</i>	
162	7.22	0.000105
446	13.23	0.000100
581	14.98	0.000100

(6) Picric acid solution	25 c.c.
N/10-KMnO <sub>4</sub>	50 c.c.
N/5-sulphuric acid	10 c.c.
	85 c.c.
+ water	255 c.c.

$k = \frac{4}{(30-25)t} \log_{10} \frac{5(30-x)}{6(25-x)}$		
<i>t.</i>	<i>x.</i>	
213	6.85	0.0000995
563	12.50	0.0000951

The bimolecular constant diminishes somewhat with dilution.

2:4:6-Trinitro-*m*-cresol.—This was prepared by the thorough nitration of *m*-cresol (98 per cent.), and recrystallised three times from alcohol. A solution containing 0.7150 gram per litre was employed.

- (8) 25 c.c. Trinitrocresol solution.  
 50 c.c.  $N/10\text{-KMnO}_4$ .  
 10 c.c.  $N/5\text{-Sulphuric acid}$ .

Amount of oxygen used up in terms of c.c.		$k = \frac{1}{(30-25)t} \log_{10} \frac{5(30-x)}{6(25-x)}$
Time in minutes.	$N/10\text{-Na}_2\text{S}_2\text{O}_3$ .	
$t$ .	$x$ .	
30	0.75	—
77	1.85	0.0000149
86	2.05	0.0000149
246	5.05	0.0000146
405	7.25	0.0000141
592	9.25	0.0000137
1006	12.53	0.0000134
1355	14.23	0.0000120
$\infty$ (theor.)	25.0	—
		Mean 0.0000141

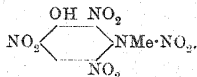
The results are completely parallel to those obtained with picric acid—the same bimolecular law and the same slight decrease in the velocity constant with time. This similarity in the dynamics of the two reactions shows, as one would expect, that a preliminary oxidation of the methyl to the carboxyl group does not disturb matters.

The ratio of the mean values of  $k$  is, then, a measure of the relative stability of the two compounds. We have:

$$\frac{k \text{ for trinitrocresol}}{k \text{ for picric acid}} = \frac{0.0000141}{0.000119} = 0.118,$$

that is, trinitrocresol is only 0.118 times as reactive towards potassium permanganate as picric acid, or is 8.5 times as stable as picric acid.

2:4:6-Trinitro-3-methylnitroaminophenol,



It was thought of interest to examine this compound as an example of a very heavily substituted phenol. It was prepared by the nitration of methylaniline in the presence of excess of concentrated sulphuric acid, followed by hydrolysis of the tetranitro-methylnitroamino-compound, which is one of the principal primary products. It was purified by several recrystallisations from acetone and from water, and its purity checked by acidimetric titration. A solution containing 0.757 gram per litre was employed.

(9) 25 c.c. Solution.  
 50 c.c.  $N/10\text{-KMnO}_4$ .  
 10 c.c.  $N/5\text{-Sulphuric acid}$

Time in minutes. <i>t</i> .	<i>x</i> .	$k = \frac{1}{(30 - 25)t} \log_{10} \frac{5(30 - x)}{(25 - x)}$
180	2.55	0.00000904
351	4.43	0.00000872
372	4.60	0.00000861
1485	11.90	0.00000825
		Mean 0.00000865

$$\frac{k}{k_{\text{picric}}} = \frac{0.00000865}{0.000119} = 0.0725.$$

The reactivity towards potassium permanganate is thus 0.0725 times that of picric acid, or the compound is 13.8 times as stable. Here, again, the similarity between the dynamics of this reaction and the picric acid reaction may be taken to show that the side-chain does not suffer attack before the ring is broken. (See Fig. II.)

#### *Dinitrophenols.*

In the case of three dinitrophenols curves of a somewhat different type were obtained. I am greatly indebted to Mr. Aldous, who kindly supplied me with pure specimens of the compounds used.

The solutions (0.3285 gram per litre) were of half the strength used in the previous experiments, and the potassium permanganate and acid correspondingly of half strength.

##### (10) 2:6-Dinitrophenol.

50 c.c. Dinitrophenol solution.  
 100 c.c.  $N/20\text{-KMnO}_4$ .  
 20 c.c.  $N/10\text{-Sulphuric acid}$ .

Time in minutes. <i>t</i> .	Amount of oxygen used up in terms of c.c. $N/10\text{-Na}_2\text{S}_2\text{O}_3$ . <i>x</i> .	<i>x/t</i> .
5	3.40	0.680
7.7	5.35	0.693
10	7.05	0.705
15.5	11.00	0.709
18.3	13.17	0.720
20	14.48	0.724
27.3	17.70	—
44.6	21.5	—
330	24.25	—
$\infty$ (theor.) for complete oxidation to carbon dioxide, nitric acid, and water.	25.0	—

##### (11) 2:4-Dinitrophenol.

50 c.c. Dinitrophenol solution.  
 100 c.c.  $N/20\text{-KMnO}_4$ .  
 20 c.c.  $N/10\text{-Sulphuric acid}$ .

Time in minutes. <i>t</i> .	Amount of oxygen used up in terms of c.c. $N/10\text{-Na}_2\text{S}_2\text{O}_3$ . <i>x</i> .	<i>x/t</i> .
11.3	0.26	—
150	5.60	0.0373
206	8.0	0.0388
307	11.60	0.0378
422	15.86	—
$\infty$	25.0	—

- (12) 2:5-Dinitrophenol.  
 50 c.c. Dinitrophenol solution.  
 100 c.c.  $N/20\text{-KMnO}_4$ .  
 20 c.c.  $N/10\text{-Sulphuric acid}$ .

Time in minutes.	Oxygen used up in terms of c.c.	
	$N/20\text{-Na}_2\text{S}_2\text{O}_3$	$x/t$
16	4.67	0.292
23.5	6.67	0.284
31	9.12	0.294
41	12.45	0.304
55	14.57	0.265
68	16.87	—
87	19.00	—
155	21.79	—
$\infty$	25.0	—

The form of the curves is quite different from that obtained with picric acid. The reactions are autocatalytic, a point which will be referred to again later. The approximate constancy of  $x/t$  over a considerable range has little theoretical bearing, but enables the initial velocity to be calculated in each case.

Initial rate of oxidation in c.c. per minute for 2:6-dinitrophenol=0.705.

Initial rate of oxidation in c.c. per minute for 2:4-dinitrophenol=0.0379.

Initial rate of oxidation in c.c. per minute for 2:5-dinitrophenol=0.294.

The corresponding initial rate for picric acid in the same units may be found by evaluating  $dx/dt$  for  $t=0$  from the expression in Expt. 4 (half strength picric acid):

$$\frac{2}{(30-25)t} \log_{10} \frac{5(30-x)}{6(25-x)} = k_2 = 0.000110,$$

whence

$$\left(\frac{dx}{dt}\right)_0 = 0.0950.$$

Approximate experiments further give a lower limit for the initial rates in the case of phenol and some mono-derivatives. The results are combined in the table below:

Compound.	Relative rate of oxidation.	Relative stability of ring.
Phenol	> 500	< 0.002
Salicylic acid		
<i>o</i> -Nitrophenol	> 250	< 0.004
<i>m</i> -Nitrophenol		
<i>p</i> -Nitrophenol		
2:6-Dinitrophenol	7.4	0.135
2:4-Dinitrophenol	0.40	2.50
2:5-Dinitrophenol	3.09	0.324
Picric acid	1.00	1.00
2:4:6-Trinitro- <i>m</i> -cresol	0.118	8.5
Trinitromethylnitroaminophenol ...	0.073	13.8



Taking into consideration the nature of the curves, it is thought that these figures give a true measure of the relative stability of the ring in the various compounds. If the initial velocity were in any case that due to the formation of another aromatic derivative indications of consecutive reactions would be found. In the only cases where these were found, namely, phenol and its mono-derivatives, the first rapid change was far too profound to be other than a complete decomposition of the aromatic nucleus.

In general, whilst phenol and its mononitro- and carboxy-derivatives are extraordinarily unstable towards potassium permanganate, the more heavily substituted compounds have acquired considerable stability. There is no definite connexion between rate of oxidation and degree of ionisation. The instability of phenol renders a true aromatic constitution improbable. It may be provisionally suggested that the reactivity is due to the production of

the tautomeric keto-form,  $\cdots\text{O}:\text{C} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{H}_2$ , or, in accordance with

the principle of Baly and Stewart, to the actual oscillation between this and the normal form. Heavy substitution might be expected to inhibit tautomerisation and to depress the reactivity. On this view the autocatalytic reaction in the case of the dinitrophenols could be simply explained. The yellow solutions of these compounds are decolorised by moderate amounts of sulphuric acid. This may well be due to the repression of a quinonoid keto-form. As oxidation proceeds sulphuric acid enters into the reaction, and the keto-form can reappear. Hence the acceleration.

In conclusion, I wish to thank Mr. D. H. Nagel, M.A., for the interest he has taken in these experiments.

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### CVIII.—*Chloropicrin. Part I.*

By JOHN ADDYMAN GARDNER and FRANCIS WILLIAM FOX.

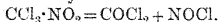
WHEN commercial chloropicrin, purified by distillation in a current of steam and dried over calcium chloride until it no longer restores the blue colour to anhydrous copper sulphate, is distilled under atmospheric pressure, it boils at about  $112^{\circ}$ , and a small amount of a yellowish-red gas, recalling in appearance diluted nitrous fumes,

is always evolved which is seen in the atmosphere of the condenser and receiver. After several redistillations the distillate and the chloropicrin remaining in the flask were found on analysis to contain the same percentage of chlorine.

No mention of this phenomenon could be found in the literature. Stenhouse (*Annalen*, 1848, **66**, 241) states that the substance distills unchanged at  $120^{\circ}$ , and can be heated to  $150^{\circ}$  without undergoing decomposition, but if the vapour is passed through a heated glass flask, at a temperature below red heat, it decomposes completely, chlorine and nitric oxide being evolved and a quantity of perchloroethane being deposited in the cooler part of the flask. Hofmann (*Annalen*, 1866, **139**, 111) gives the boiling point  $112^{\circ}$ , and Thorpe (T., 1880, **37**, 198)  $111.91^{\circ}$ , but neither observer mentions any decomposition. Cossa (*Gazzetta*, 1872, **2**, 181) gives the boiling point  $112.8^{\circ}$ , and states that the substance explodes when rapidly heated or when the vapour is led into a red-hot tube. Levy and Jedlicka (*Annalen*, 1888, **249**, 86) state that bromopicrin explodes on distillation under the ordinary pressure, giving red fumes, but that it can be distilled unchanged under diminished pressure. In the article on chloropicrin in Wurtz's "Dictionnaire de Chimie," the writer states that "elle bout à  $120^{\circ}$ ; à  $112^{\circ}$  (Hofmann): elle supporte une température de  $150^{\circ}$  sans se décomposer; surchauffée sa vapeur fait une violente explosion."

It seemed of interest, therefore, to submit the phenomenon to closer investigation.

When chloropicrin was caused to explode by heat or otherwise, a strong odour of carbonyl chloride was always noticed. This fact, together with the constancy of composition after boiling, suggested that chloropicrin at its boiling point slowly decomposes into carbonyl chloride and nitrosyl chloride:



This was found to be the case, and 200 c.c. of that liquid, kept very gently boiling, decomposed at the rate of about 2 c.c. per day.

This observation is of interest for a variety of reasons. It throws light on the rather divergent statements that have been made on the physiological activity of chloropicrin. In making experiments on this subject, the mixture of chloropicrin vapour and air to be tested on animals should be made either by atomising the liquid into the air or by evaporating at a low temperature; if the mixture were made by boiling the chloropicrin, or by bursting a bomb by any means, the atmosphere produced would contain chloropicrin vapour more or less contaminated with carbonyl chloride and nitrosyl chloride, and if the air were damp perhaps also nitrous fumes, so that a mixed result would be obtained.

It also throws light on many of the chemical reactions of chloropicrin, which is a very reactive substance. It has already been pointed out by Frankland, Challenger, and Nicholls (this vol., p. 159) that under some conditions chloropicrin is reduced quantitatively to methylamine, but under others to ammonia, etc. Obviously in the first case it is reduced as such, and in the latter the decomposition products are reduced.

There are many other reactions in which chloropicrin behaves as an oxidising agent. In some it appears to react as a nitro-compound; for instance, it can be used to replace nitrobenzene in Skraup's method of preparing quinoline, in others the results can be explained as due to the decomposition products. We hope shortly to have the honour of bringing before the Society a detailed account of some of these reactions.

This decomposition may also account for the varied yields obtained by different observers in the production of chloropicrin by the action of bleaching powder on picric acid. By proper attention to the proportions of the reagents and the conditions of reaction yields of 180—190 per cent. of the picric acid used can easily be obtained on a technical scale,\* but if the optimum conditions are not strictly adhered to the yield may easily sink to 130 per cent., or even to 114 as given originally by Hofmann, or less.

#### EXPERIMENTAL.

Chloropicrin, in quantities of about 200 c.c., was boiled, on a sand-bath, in a 300 c.c. flask with a long neck and provided with a long reflux condenser. The end of the condenser was connected to a series of wash-bottles containing the reagents for absorbing the

\* The proportions found to be best for obtaining yields of about 180 per cent. were 10 parts of picric acid to 100 parts of bleaching powder. The exact proportion, however, depends on the quality of the latter. The material used generally contained about 33 per cent. of available chlorine. The method adopted was to carry out a trial distillation with the above proportions. If it was found in the trial distillation that the effluent was at all yellow the amount of picric acid was lessened. If it was found that there was any tendency to frothing, a little extra was added. This was found to be a much more satisfactory method of work than attempting to estimate each batch of bleaching powder. The best conditions for the reaction are for the bleaching liquor to be about 30°, when on the addition of solid picric acid the temperature very rapidly rises to distilling point and steam is only used in the final stage of the reaction to carry over the last traces of chloropicrin. Contrary to statements frequently made, no artificial means of evading frothing is of any practical use. Once frothing commences badly, the yield steadily diminishes. On the large scale, the only way of destroying froth is to add a further small quantity of solid picric acid, a somewhat unpleasant, not to say dangerous operation.

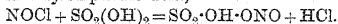
products of decomposition. The various parts of the apparatus were joined either by ground-glass joints or by sealing in the blow-pipe.

In the earlier experiments the wash-bottles were charged with 40—50 per cent. potassium hydroxide solution to absorb the whole of the products of decomposition. At the end of an experimental period the contents of the bottles were diluted to definite volume and estimations were made of the carbonate, nitrite, and chloride present. The method did not prove quite satisfactory, as the connecting tubes were apt to become clogged with crystalline matter deposited from the concentrated alkaline solution. It also proved difficult to obtain complete absorption of the carbonyl chloride. The latter difficulty was overcome by charging the last bottle with  $N/2$ -alcoholic potassium hydroxide. Owing to the large bulks of concentrated alkali hydroxide required, and the long duration of the experiments, it proved troublesome to make very exact corrections for the chlorides and carbonates contained in the original potassium hydroxide.

In two experiments the ratio  $\text{CO}_2:\text{NO}_2:\text{Cl}$  was found to be 1:1.003:2.14 and 1:0.993:2.42 respectively. The theoretical ratio is 1:1.046:2.42.

In subsequent experiments the constituents of the mixture were absorbed separately.

The first wash-bottle was charged with concentrated sulphuric acid, which absorbed the nitrosyl chloride, producing hydrogen chloride and nitrosylsulphuric acid,



The mixture of hydrogen chloride and carbonyl chloride was then passed into bottles containing either benzene or toluene to absorb the carbonyl chloride. The hydrogen chloride was either allowed to escape, or in some experiments was collected in copper sulphate solution.

#### *Examination of the Sulphuric Acid Liquor.*

The contents of the first bottle had all the properties of a solution of nitrosylsulphuric acid in concentrated sulphuric acid. It did not, however, crystallise on long keeping in the ice-chest, even when the nitrosyl chloride had been passed through up to the limits of the capacity of the acid for efficient absorption. The liquor was therefore submitted to fractional distillation under diminished pressure. It was not possible to obtain a complete separation of the sulphuric acid from the nitrosylsulphuric acid, since some of the latter passed over even in the first runnings which, on keeping in the air for a short time, became distinctly blue. When about half

the acid had passed over, the sides of the receiver began to be coated with the well-known chamber crystals. On further distillation solid deposited in the condensing tube, the liquid in the receiver crystallised, and the residue in the distilling flask solidified on cooling.

This crystalline matter was purified, so far as possible, from free sulphuric acid by keeping it for many days on porous tile over sulphuric acid in a desiccator, and occasionally scraping on to fresh tile. In this way a quantity of approximately pure nitrosylsulphuric acid was obtained as a white, crystalline mass, which began to soften at about  $30^{\circ}$  with evolution of vapour. The crystals dissolved in a trace of water to a blue liquid, were readily soluble in concentrated sulphuric acid, and on dilution with much water gave a solution of sulphuric and nitric acid. The preparation contained no trace of chlorine.

A specimen was analysed by estimation of sulphuric acid after dissolving in water, and by titration of the solution in concentrated sulphuric acid into permanganate (Found,  $\text{SO}_3 = 63.86$ , oxygen required  $= 11.93$ ; Calc.,  $\text{SO}_3 = 63.01$ ; oxygen required  $= 12.59$  per cent.).

#### *Examination of the Benzene or Toluene Solutions.*

A toluene solution (114 c.c.), containing carbonyl chloride liberated in four days, was shaken with 150 c.c. of 40 per cent. potassium hydroxide solution in a closed bottle in the shaking machine for six hours. The alkaline layer was then made up to 250 c.c. Estimations of chloride and carbonate were made in this, and also in a control sample of potassium hydroxide, similarly treated.

- (1) 25 c.c. gave 2.6954 AgCl and 0.4487  $\text{CO}_2$ .
- (2) 25 c.c. ,, 2.6911 AgCl.
- (3) 26 c.c. control gave 0.0397 AgCl and 0.0372  $\text{CO}_2$ .

Ratio  $\text{Cl}:\text{CO}_2 = 1:0.6266$ .

Theory for  $\text{CoCl}_2 = 1:0.6205$ .

This toluene solution, from the rate of decomposition given below, should have contained between 8.4 and 11.2 grams of carbonyl chloride. It actually contained from the above analysis 9.16 grams.

In another experiment about 500 c.c. of benzene, containing the carbonyl chloride produced in forty-one days, were boiled in a flask with a reflux condenser, the upper end of which was connected to a worm condenser and receiver, both cooled by a freezing mixture of ice and salt, when between 7 and 8 c.c. of liquid carbonyl chloride, boiling at  $8^{\circ}$ , were obtained.

Much carbonyl chloride escaped condensation under these conditions, and a considerable amount remained in the benzene. The residual solution was shaken with concentrated aqueous ammonia and the aqueous layer evaporated to dryness. The crystallised residue was mainly ammonium chloride, but a trace of carbamide was isolated from it in the usual manner, and identified by its crystalline form, the biuret test, and the evolution of ammonia on treatment with soya-bean urease.

For the further identification of the carbonyl chloride it was converted into benzophenone by the Friedel and Crafts method. For this purpose about 250 c.c. of benzene, containing the carbonyl chloride evolved in seven to eight days, were used.

The benzophenone crystallised from alcohol in the usual characteristic form, and melted at  $48.5-49^{\circ}$ . A mixture with a specimen from another source showed no change in melting point. The yield was about 62 per cent. of the theoretical, and was similar in order to that recorded by Friedel and Crafts (*Ber.*, 1877, 10, 1856).

Dimethyl-*p*-aminobenzoic acid was also obtained, with other products, in needle-like crystals melting at  $235^{\circ}$ , by heating a toluene solution with dimethylaniline in a closed flask at  $130^{\circ}$  for several hours, and then distilling off the toluene in a current of steam.

#### *Examination of the Chloropicrin left after Prolonged Heating.*

This was yellow, and completely volatile in steam, leaving no residue. On distillation the following fractions were obtained: up to  $103^{\circ}$ , 3 grams;  $103-108^{\circ}$ , 5.2 grams;  $108-112^{\circ}$ , 278.7 grams; residue in flask, 3.8 grams. It was evidently unchanged chloropicrin.

The chloropicrin, after distillation in a current of steam, contained some nitrous fumes in solution, which were given off at the beginning of distillation and coloured the first fraction brown. These were easily displaced by a current of air.

Fraction 3 was found to contain Cl=64.79, and two specimens of the commercial chloropicrin used 64.82 and 64.92 respectively.  $\text{CO}_2\text{NCl}_3$  requires Cl=64.71 per cent.

#### *Rate of Decomposition.*

Chloropicrin (200 c.c.) was gently boiled for sixty-eight days, and 58 c.c. remained at the end. It decomposed therefore at the rate of 2.088 c.c. or 3.487 grams per day, and produced 2.099 grams of carbonyl chloride per day.

In another experiment in which the chloropicrin was kept rapidly

boiling, 64.6 grams of carbonyl chloride, determined from the increase in weight of the toluene wash-bottles, were obtained in twenty-three days, a rate of decomposition giving 2.8 grams per day.

In order to ascertain whether this decomposition could be attributed to traces of moisture, the chloropicrin, which had been dried over calcium chloride and gave no reaction with anhydrous copper sulphate, was allowed to remain for several days with a large excess of phosphoric oxide. It was then transferred to the carefully dried apparatus and heated as described. Decomposition took place, and 8 grams of carbonyl chloride were obtained in ninety-one hours, a rate of decomposition giving 2.097 grams per day, and of much the same order as before. The residual chloropicrin was found to contain Cl = 64.65 per cent.

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CIX.—*The Temperature of Critical Solution of a Ternary Mixture as a Criterion of Purity of n-Butyl Alcohol. The Preparation of Pure n-Butyl Alcohol.*

By KENNEDY JOSEPH PREVITÉ ORTON and DAVID CHARLES JONES.

SINCE the introduction of the fermentation process, *n*-butyl alcohol prepared from starch has become a common industrial product which will certainly find a use in chemical industry and not improbably as a solvent.

We have examined some of its solubility relations with the object of finding in the temperature of critical solution ("c.s.t.") with other media a rapid and certain method of following the course of a fractionation by which butyl alcohol is being purified, or of detecting the presence of impurity in a specimen of butyl alcohol. It was pointed out in a previous paper (this vol., p. 1055), on a similar use of this method for toluene, that different impurities both present together in the liquid under investigation may have an opposite effect on the c.s.t. as on other physical properties. Usually, however, the c.s.t. of a number of fractions

into which the liquid has been divided by distillation will reveal the true condition of the liquid.

The solubility relations with water of the three isomerides of *n*-butyl alcohol have been studied by Alexéev (*Ann. Phys. Chem.*, 1886, [iii], **28**, 305) and Timmermans (*Zeitsch. physikal. Chem.*, 1907, **58**, 129).

*tert*-Butyl alcohol is miscible with water at the ordinary temperature, whilst the solubility curve of *isobutyl* alcohol has a c.s.t. at 130° (Alexéev), and *sec*-butyl alcohol one at 113.7° (Alexéev, Timmermans). Both curves show a maximum of mutual insolubility in the neighbourhood of 50°. The solubility curve of *n*-butyl alcohol has not been followed up to the c.s.t., which will be well above 150°, but it shows a similar maximum of insolubility at about 50°.

As a criterion of purity, the binary c.s.t. with water would not only be at an inconvenient temperature and pressure, but useless for detecting the commonest impurity, namely, water. No other binary mixture seems available, for although ethyl alcohol forms a binary with petroleum, which has found a similar application in Crismer's hands, and methyl alcohol with carbon disulphide, the higher alcohols are completely miscible with these liquids. A ternary mixture was therefore sought.

A 14 per cent. (13.994 grams per 100 grams of solution) solution of hydrochloric acid was chosen, as both very convenient for our purpose and sufficiently sensitive; it gives an upper c.s.t. at 43.55° and a lower at 9.6° with *n*-butyl alcohol.

*n*-Butyl alcohol is completely miscible with concentrated hydrochloric acid (20 per cent.) at the ordinary temperature (Lieben and Rossi, *Annalen*, 1871, **158**, 137). The presence of hydrochloric acid causes a contraction of the solubility ring of the system butyl alcohol-water, in the same way as does ethyl alcohol that of the system methyl ethyl ketone-water (Bruni, *Atti R. Accad. Lincei*, 1899, [v], **8**, 141).

Fig. 1 represents the change in the system *n*-butyl alcohol-water when hydrogen chloride is introduced. The solubility ring, *KK'*, of water and butyl alcohol has, as yet, been followed over only a small section of the lateral portions; the intervention of the solid-liquid curve, *sL*, prevents the realisation of the lower c.s.t. *K'*. When hydrogen chloride is present, the ring contracts; *L'*, the lower c.s.t., appears above the ice line, and *L*, the upper, is now at a lower temperature. As the concentration of the hydrogen chloride increases, the ring further contracts until, finally, miscibility is complete.



Aqueous sulphuric and nitric acids give upper ternary c.s.t.'s, but no lower c.s.t.'s were observed:

Sulphuric acid (24 per cent.) gave a c.s.t. at  $8^{\circ}$ , nitric acid (35 per cent.) at  $5^{\circ}$ .

Sulphuric acid (20 per cent.) gave a c.s.t. at  $80^{\circ}$ , nitric acid (31 per cent.) at  $37^{\circ}$ .

The method of determining the c.s.t., and the apparatus employed, have been fully described in an earlier paper (*loc. cit.*).

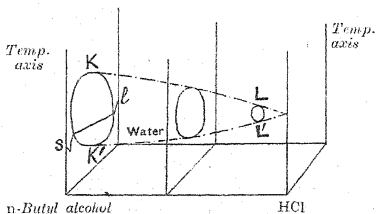
The quantities of the acid solution and butyl alcohol which gave very vividly the critical phenomena are:

Acid solution, 1 c.c.; butyl alcohol, 0.4958 c.c.

Pipettes of the type used for toluene were constructed and carefully calibrated to deliver these quantities with that exactness which we have shown (*loc. cit.*) to be so necessary.

*The n-Butyl Alcohol.*—In order to prepare a pure *n*-butyl

FIG. 1.



alcohol, several specimens from various sources have been examined. The untreated alcohols gave c.s.t.'s with the standard aqueous hydrochloric acid varying between such wide limits as an upper c.s.t. of  $84^{\circ}$  and complete miscibility, whereas pure butyl alcohol gives the value  $43.55^{\circ}$ .

Most of these crude alcohols, after treatment with ordinary chemical reagents—dilute acids to remove bases, sodium hydrogen sulphite to remove aldehydes and ketones, and boiling sodium hydroxide to decompose esters—and subsequent distillation, were found capable of giving a large percentage of material, the various fractions of which, on redistillation, gave the same c.s.t. about  $43^{\circ}$ . Some of the material, however, which was homogeneous so far as could be tested by distillation, gave c.s.t.'s varying widely from this value; as one example, the c.s.t. was about  $50^{\circ}$ , and as another about  $60^{\circ}$ .

As examples of the behaviour of these crude butyl alcohols on distillation, the following may be cited:

(1) A crude specimen (1000 c.c.) had an initial c.s.t. of 44.8°. After drying with potassium carbonate, the c.s.t. was reduced to 37.8°. On distillation through an eight-bulb still-head, the main fraction of 550 c.c., boiling at 116.5°, gave a c.s.t. of 46.8°.

After chemical treatment and redistillation, a considerable quantity of homogeneous material could be obtained from this main fraction (as well as from other specimens which had been similarly treated), the c.s.t. of which was 43—44°.

An alcohol (1000 c.c.) from another source, which was remarkable as being initially completely miscible with the standard hydrochloric acid, on mere distillation through an eight-column Young and Thomas dephlegmator furnished 750 c.c. of a homogeneous material giving a c.s.t. of 43°.

Two other examples may be mentioned of specimens which give after a similar treatment quite different values of the c.s.t.

Table I shows a record of fractionation of a specimen giving an initial c.s.t. of 66.7°.

TABLE I.

Temperature.	Volume of distillate.	Critical point.	Temperature.	Volume of distillate.	Critical point.
116.0°	10 c.c.	63.1°	116.3°	10 c.c.	61.5°
116.2	10 ..	61.7	116.4	10 ..	61.7
116.3	10 ..	59.8	116.4	10 ..	62.4
			116.5	10 ..	64.6
			Residue.	7 ..	above 90

Treatment with chemical reagents left the value of the c.s.t. unaltered.

The fractionation of another specimen, which gave after fractionation a homogeneous material with a c.s.t. of about 50°, is cited below (table II).

One was thus unable, in the absence of a pure synthetic alcohol, to decide definitely whether the homogeneous material, giving a c.s.t. of 43°, contained an impurity impossible to remove by distillation, which lowered the c.s.t., or whether the homogeneous material, giving a much higher c.s.t., contained impurities such as paraffins of similar boiling point, impossible to remove by distillation or chemical treatment, which raised the c.s.t.

It has been no simple matter to find a derivative of *n*-butyl alcohol which would provide a means of obtaining the pure substance. The derivative should preferably be a crystalline solid, into which the alcohol could be readily converted, and from which

as readily recovered without chemical change of the alcohol. The sodium salt of butyl salicylate meets these conditions.

A large quantity of the alcohol, the fractionation of which is shown in the table (table II), was converted into the salicylate;

TABLE II.

Fraction.	Volume.	Critical solution point.
1	40 c.c.	57.0°
2	252 "	50.0
3	415 "	49.3
4	295 "	49.0
5	28 "	50.05

the sodium salt is prepared by dropping the ester into a slight excess of 10 per cent. sodium hydroxide which is being vigorously stirred. The sodium salt crystallises out immediately; it is collected and freed from adherent liquor by pressure. The salt is reconverted into the ester by slowly adding both 10 per cent. hydrochloric acid and the solid salt to a large volume of cooled water which is being stirred. This process is repeated with the recovered ester. The ester is then hydrolysed by aqueous sodium hydroxide, and the butyl alcohol, saturated with water, is dried with potassium carbonate and distilled. Overheating, which would in itself lead to contamination, was avoided by using an oil-bath in this and other distillations. The table shows the values of the c.s.t.'s of the fractions in the final distillation.

TABLE III.

Fraction.	Weight of fraction. Grams.	Critical solution point.
1	10	43.7°
2	27	43.55
3	27	43.55
4	30	43.5
5	20	43.5
Residue	about 5	—

It is seen that the material is now remarkably homogeneous. This *n*-butyl alcohol, which gives an upper c.s.t. at 43.55° and a lower c.s.t. at 9.6° with 13.994 per cent. hydrochloric acid, has  $D_{44}^{20}$  0.81617.

*Relation between the Concentration of Hydrochloric Acid and the Ternary Critical Solution Temperatures observed with n-Butyl Alcohol.*

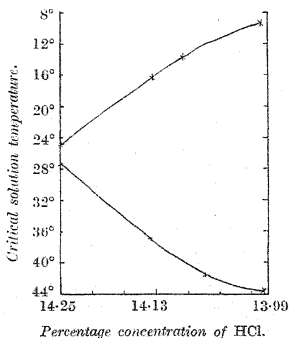
The c.s.t. is extremely sensitive to change in the concentration of the hydrogen chloride. Hydrochloric acid solutions of various

strengths were made up, and a definite volume (1 c.c.) was added to a definite volume of *n*-butyl alcohol (0.4958 c.c.) in the experimental tube. The table shows the experimental values, and Fig. 2 the curves constructed from them.

TABLE IV.

Concentration of acid. (Grams in 100 grams of solution.)	Critical solution points.	
	Upper.	Lower.
13.994	43.55°	9.6°
14.068	41.8	12.1
14.133	36.8	16.3
14.248	27.4	25.0

FIG. 2.



So small a change in the concentration of the hydrochloric acid as 0.254 per cent. alters the upper c.s.t. by 16.15°, and the lower by 15.4°. This great sensitiveness would afford a means of ascertaining whether two solutions of hydrochloric acid within a small range were of accurately identical concentration.

The measurement of the concentration of the hydrochloric acid solution has required exceptional care. As the most accurate process, a determination was chosen based on the measurements of the iodine (by *N*/20-thiosulphate, and starch indicator), set free from a mixture of potassium iodide and iodate, in which the amount of iodate is very accurately known. (Fuller details of the procedure will appear, it is hoped, in another place.) This method has been fully tested, and the accuracy with which

the solution of hydrochloric acid has been measured is represented by the number  $14.248 \pm 0.001$  per cent. This mean error corresponds with a difference of  $0.05^\circ$  in the c.s.t. of the system *n*-butyl alcohol-water-hydrochloric acid. This particular solution of hydrochloric acid was used throughout the experiments on the purification of *n*-butyl alcohol.

Obviously, in preparing an aqueous hydrochloric acid for the purpose of following the purification of *n*-butyl alcohol, the concentration of the hydrochloric acid used need not be known with such accuracy. With the ordinary volumetric solutions, accurately standardised, and by using standard burettes, the concentration of the hydrochloric acid can be ascertained as  $14.0 \pm 0.02$  per cent., and by a gravimetric analysis as  $14.0 \pm 0.005$  per cent. The divergence in the c.s.t. corresponding with this mean error will amount to  $1^\circ$  in the one and to  $0.25^\circ$  in the other.

*The Sensitiveness of the Critical Solution Temperature to Impurities.*

*Water.*—Water is one of the components of the system, and its effect as an impurity in the *n*-butyl alcohol is seen from table V to be comparatively slight; 1 per cent. of water raises the upper c.s.t. by  $1^\circ$ . Here, as in all these experiments on the effects of impurities, the concentration of the hydrogen chloride remains constant, the composition of the system only altering in the relative proportions of *n*-butyl alcohol and water. The immensely different effect produced when the concentration of the *n*-butyl alcohol remains constant, while the ratio  $\frac{\text{concentration of HCl}}{\text{concentration of H}_2\text{O}}$  is varied, is seen from the results on the relation between the concentration of the hydrochloric acid and the c.s.t., when a change of 0.25 per cent. leads to a fall or rise in the c.s.t. of  $16^\circ$ .

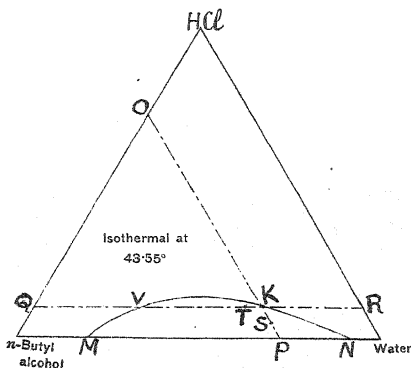
An explanation of this divergence is forthcoming from a consideration of the isothermal diagram at  $43.55^\circ$ .

In Fig. 3, *M* (80 per cent. of butyl alcohol) and *N* (8 per cent. of butyl alcohol) represent, roughly, the composition of a saturated solution of water in *n*-butyl alcohol and of alcohol in water at this temperature. *K* represents the composition of the system at the ternary c.s.t. at  $43.55^\circ$ . (HCl=10.15; *n*-butyl alcohol=27.45; water=62.4 per cent.)

From these results, it appears that the binodal curve has the general form shown—a curve with a very flat top. The line *OKP* represents the composition of the system with constant concentration of *n*-butyl alcohol, and the line *QKR* the composition of

the system with constant concentration of hydrochloric acid. From *K*, movement along *KSP*, that is, decrease in the concentration of the hydrochloric acid, with a corresponding increase in the concentration of water, the concentration of the alcohol being constant, brings the system into the heterogeneous region; by movement along *KTQ*, that is, decrease in the concentration of water, with a corresponding increase in the concentration of the alcohol, the concentration of the hydrochloric acid being constant, the system is brought again into the heterogeneous region, but at

FIG. 3.



no point is it far removed from the binodal curve, which it again cuts at *V*.

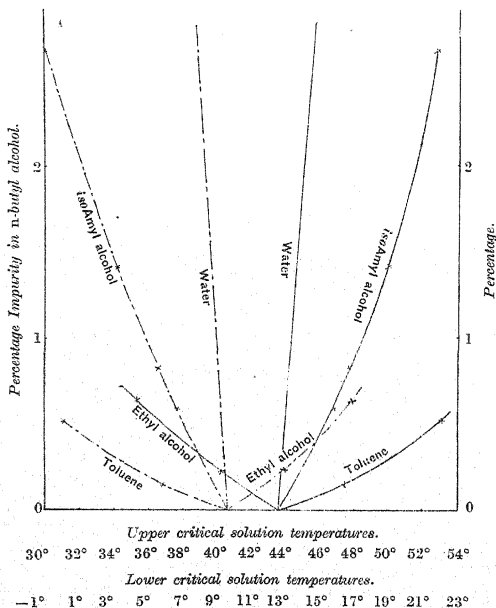
Let  $\frac{KT}{\text{water}}$  represent a 1 per cent. change in the ratio  $\frac{n\text{-butyl alcohol}}{\text{water}}$ , the concentration of the hydrochloric acid being constant, then  $\frac{KS}{\text{water}}$ , which equals  $\frac{KT}{\text{water}}$ , represents a 1 per cent. change in the ratio  $\frac{\text{hydrochloric acid}}{\text{water}}$ , the concentration of the alcohol being constant. *S* is obviously very much further removed from the binodal surface than *T*. Hence, as a result of the form of the binodal curves, a far larger change of temperature would be required to bring the system at *S* on to a binodal curve than the system at *T* on to a curve.

The results obtained with the other substances, namely, toluene,

ethyl alcohol, and amyl alcohol, which have been tested, appear in table V and Fig. 4.

The c.s.t. is extremely sensitive to the presence of such a substance as toluene, the solubility of which in water so greatly differs from that of *n*-butyl alcohol. One per cent. of toluene in the butyl alcohol raises the upper and depresses the lower c.s.t. by 19°. Paraffin, which is less soluble, has a still greater effect.

FIG. 4.



*Discontinuous curves represent the effect of impurity on the lower c.s.t.*

*Continuous curves represent the effects on the upper c.s.t.*

The c.s.t. is thoroughly sensitive to the presence of homologues. One per cent. of ethyl alcohol lowers the upper c.s.t. by 11°, and 1 per cent. of amyl alcohol raises the upper c.s.t. by 5°, correspond-

ing alterations being observed in the lower c.s.t. Rough experiments with *n*-propyl, *isobutyl*, and *sec.*-butyl alcohols show a less, but still an appreciable, effect. One per cent. of *n*-propyl alcohol lowers the c.s.t. by  $6.1^{\circ}$ , 1 per cent. of *isobutyl* alcohol by  $0.7^{\circ}$ , and 1 per cent. of *sec.*-butyl alcohol by  $1.9^{\circ}$ . The relations of the c.s.t.'s of isomerides are being more fully examined.

The values of the c.s.t. in table V were obtained when the quantities of the two constituents delivered respectively by the two pipettes were used, that is, 1 c.c. of the standard hydrochloric acid and 0.4958 c.c. of impure *n*-butyl alcohol. The "percentage" of admixture is by weight in the *n*-butyl alcohol.

TABLE V.

Water present, per cent.	0	2.677	2.796	10.75	4.034
Upper c.s.t. ....	43.55°	45.7°	46.2°	52.35°	47.95°
Lower c.s.t. ....	9.6	8.2	7.9	3.0	6.5
Toluene present, per cent. ....	0	0.1422	0.3157	0.5077	
Upper c.s.t. ....	43.55°	47.4°	50.1°	53.2°	
Lower c.s.t. ....	9.6	5.8	3.15	-1.15	
Amyl alcohol present, per cent. ....	0	0.5910	0.8366	2.666	1.415
Upper c.s.t. ....	43.55°	46.95°	47.6°	53.8°	50.1°
Lower c.s.t. ....	9.6	6.75	5.8	-0.9	3.25
Ethyl alcohol present, per cent. ....	0	0.6288	0.2381		
Upper c.s.t. ....	43.55°	35.3°	40.1°		
Lower c.s.t. ....	9.6	16.8	12.8		

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## CX.—The Action of Grignard Reagents on the Esters of Certain Dicarboxylic Acids.

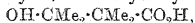
By HARRY HEPWORTH.

THE action of Grignard reagents on the esters of the simpler saturated aliphatic dicarboxylic acids has been the subject of several investigations. Valeur (*Compt. rend.*, 1901, **132**, 833) obtained ditertiary glycols by the action of magnesium methyl iodide and magnesium ethyl iodide on ethyl oxalate, ethyl malonate, and ethyl succinate, and somewhat later (*Compt. rend.*, 1903, **136**, 694) prepared benzopinacolone and tetraphenylbutanediol by the



action of magnesium phenyl bromide on methyl oxalate and ethyl succinate respectively. Dilthey and Last (*Ber.*, 1904, **37**, 2639) claimed to have prepared  $\beta$ -benzopinacolin from ethyl oxalate, and magnesium phenyl bromide, and diphenylphenacetylcarbinol,  $\text{COPh}\cdot\text{CH}_2\cdot\text{CPh}_2\cdot\text{OH}$ , from ethyl succinate in a similar way. Valeur, however, still claimed that the product of the action of magnesium phenyl bromide on methyl or ethyl oxalate is benzopinacone (*Compt. rend.*, 1904, **139**, 480). Again, Harries (*Annalen*, 1905, **343**, 363) prepared  $\beta\epsilon$ -dimethylhexane- $\beta\epsilon$ -diol,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{OH}$ , by the interaction of magnesium methyl iodide and ethyl succinate. In all these investigations the experimental conditions have been such as would favour attack on both carboxyalkyl groups by the Grignard compound employed, with the result that almost invariably fully substituted glycols or compounds of an analogous nature have been produced.

An exception arises in the work of Slavjanov (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 140), who, during the course of some experiments on the preparation of hexamethylcyclopropane, incidentally obtained some  $\beta$ -hydroxy- $\alpha\alpha\beta$ -trimethylbutyric acid,



by the action of magnesium methyl iodide on methyl dimethylmalonate. The only other evidence of selective action of Grignard reagents on one of the two carboxyalkyl groups of the esters of the simpler aliphatic dicarboxylic acids appears to be that of Egorova (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1454), who acted on ethyl oxalate with magnesium *tert.*-butyl chloride, and obtained, amongst other products,  $\alpha$ -hydroxy- $\beta\beta$ -dimethylbutyric acid,  $\text{CMe}_3\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ , and  $\alpha$ -ethoxy- $\beta\beta$ -dimethylbutyric acid,  $\text{CMe}_3\cdot\text{CH}(\text{OEt})\cdot\text{CO}_2\text{H}$ ; whilst, in the hope of finding a convenient method of obtaining  $\alpha$ -ketonic acids, the action of Grignard reagents on ethyl oxalate was investigated by Inglis and Mason (*P.*, 1909, **25**, 195), but the work described in this note is incomplete and does not appear to have been subsequently published.

In view of the fact that the discrepancy between the observations of Slavjanov (*loc. cit.*) and the results of other workers might be attributed either to a form of steric hindrance exerted by the methyl-substituting groups of the ester of dimethylmalonic acid or to the fact that Slavjanov used only three equivalents of magnesium and methyl iodide, whereas Valeur, Dilthey, and Harries used at least four equivalents, it was decided to carry out experiments to ascertain whether, by suitable control, the action of the Grignard reagent on the esters of certain aliphatic dicarboxylic acids could be confined to one carboxyalkyl group.

In this connection, it is interesting to note that Grignard

reagents react in a rather anomalous and unexpected manner with ethyl acetoacetate and its alkyl derivatives. Thus Grignard has shown (*Compt. rend.*, 1902, **134**, 849) that magnesium methyl iodide and ethyl acetoacetate give methane, hydrogen, and unchanged ester, the ester thus reacting in the enolic form. On the other hand, the monoethyl derivative of ethyl acetoacetate and magnesium methyl iodide react to give some ethyl  $\beta$ -hydroxy- $\alpha$ -ethylisovalerate,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$ , whilst methyl diethylacetoacetate does not react at all. Again, McKenzie (*T.*, 1906, **89**, 380) has shown that menthyl acetoacetate reacts as though entirely enolic.

Experiments have been carried out on the action of magnesium methyl iodide and magnesium ethyl bromide on ethyl oxalate, ethyl malonate, ethyl ethylmalonate, ethyl dimethylmalonate, and ethyl succinate, using about 2.5 equivalents of magnesium and alkyl haloids to one of ester. With the exception of ethyl malonate, which appears to react entirely in the enolic form, the reaction has been so regulated as to confine the action of the Grignard compound almost completely to one carboxyalkyl group.

In these experiments it was not found necessary to prepare the Grignard reagent separately, as the best results were obtained by dropping a mixture of alkyl haloid and ester into a well-stirred and cooled mixture of magnesium powder and dry ether (compare Davies and Kipping, *T.*, 1911, **99**, 296). The mixture of alkyl haloid and ester was added at such a rate as to keep the reaction just perceptibly in progress.

In this way  $\alpha$ -hydroxyisobutyric acid and  $\alpha$ -hydroxy- $\alpha$ -ethylbutyric acid were prepared from ethyl oxalate,  $\beta$ -hydroxy- $\alpha$ -ethylisovaleric acid from ethyl ethylmalonate,  $\beta$ -hydroxy- $\alpha\alpha\beta$ -trimethylbutyric acid from ethyl dimethylmalonate, and isohexolactone and  $\gamma$ -ethyl-*n*-hexolactone from ethyl succinate.

Now Shibata has shown (*T.*, 1909, **95**, 1449) that Grignard reagents react with ortho-phthalic esters to give derivatives of phthalide, in which only one carboxyalkyl group of the phthalic ester is attacked. He compares this reaction with the production of tetra-alkylbutanediols from ethyl succinate and Grignard compounds (Valeur, *loc. cit.*), and concludes from this, together with the work of Bethmann (*Zeitsch. physikal. Chem.*, 1890, **5**, 409) on succinic acid, that in the latter compounds the two carboxyl groups are in the *trans*-position, whereas in *o*-phthalic acid the carboxyl groups are in the *cis*-position. It has now been shown that the action of the Grignard compound may be confined to one carboxyalkyl group in the case of ethyl succinate with the production of  $\gamma\gamma$ -dialkylbutyrolactones, from which it might equally well be

concluded that the two carboxyl groups in succinic acid are in the *cis*-position. All that can be safely inferred, however, seems to be that in the intermediate compounds obtained by the interaction of Grignard compounds and ethyl succinate or orthophthalic esters, the hydroxyl and carboxyalkyl groups are possibly in the *cis*-position, and in the absence of any strictly quantitative data it is somewhat hazardous to draw any conclusions as to the steric structures of succinic and phthalic acids from such observations.

#### EXPERIMENTAL.

##### *Preparation of $\alpha$ -Hydroxy- $\alpha$ -ethylbutyric Acid from Ethyl Oxalate.*

Three hundred grams of dry ether and 10 grams of magnesium powder were introduced into a wide-necked flask provided with a stirrer, dropping funnel, and condenser, and surrounded by ice. Ten grams of ethyl bromide were placed in the flask, and after the reaction had started a mixture of 73 grams of ethyl oxalate and 126 grams (2.5 mols.) of ethyl bromide was added at such a rate as to keep the reaction proceeding slowly. The rest of the magnesium, 21 grams (2.5 mols.), was added from time to time so as to keep the magnesium always in excess. Towards the end of the reaction the contents of the flask became very viscous. Stirring was continued for an hour after the whole of the magnesium had been added, after which the mixture was allowed to remain overnight at the ordinary temperature.

The mixture was then heated on a water-bath for two hours and, after cooling, ice-cold water followed by 40 per cent. sulphuric acid was slowly added until the whole of the magnesium had dissolved.

A brown oil separated, and after its removal the residue was extracted four times with ether. The oil and ethereal extract were combined, dried over anhydrous sodium sulphate, and the ether removed by distillation, when 61 grams of a brown, rather viscous oil remained.

This oil was then distilled, when about 53 grams passed over between 172° and 185°. At 210° there was evidence of decomposition and the distillation was stopped. The fraction distilling at 172—185° was fractionated in a five-pear column, when about 48 grams distilled at 174—180° and about 4 grams at 180—186°. The latter proved to be principally unchanged ethyl oxalate.

The fraction distilling at 174—180° was redistilled, when 45.5 grams (57 per cent.) of ethyl  $\alpha$ -hydroxy- $\alpha$ -ethylbutyrate distilled at 175—177° (corr.) (Frankland and Duppa, *Annalen*, 1863, 126, 109).

Sixteen grams of the ester were boiled under reflux with 5 grams

(1½ mols.) of sodium hydroxide for two hours. After cooling and acidifying, a solid separated, which was removed, and the residue extracted six times with ether. There were obtained 12 grams of an acid, which crystallised from light petroleum in long needles melting at 79·5°.

The identity of this acid with  $\alpha$ -hydroxy- $\alpha$ -ethylbutyric acid was established by conversion into its barium salt (Found, Ba=34·22; calc., Ba=34·3 per cent.) and by its conversion into the ethylisocrotonic acids on repeated distillation (Fittig, *Annalen*, 1904, **334**, 101).

*Preparation of  $\alpha$ -Hydroxyisobutyric Acid from Ethyl Oxalate.*

This was carried out on exactly the same lines as the preparation of  $\alpha$ -hydroxy- $\alpha$ -ethylbutyric acid described above, except that methyl iodide was used instead of ethyl bromide. Seventy-three grams of ethyl oxalate were treated with 30 grams (2·5 mols.) of magnesium powder and 180 grams (2·5 mols.) of methyl iodide; 39·6 grams (60 per cent.) of an oil boiling at 150—151° were obtained, and the identity of this with ethyl  $\alpha$ -hydroxyisobutyrate was confirmed by conversion of 10 grams of the ester into the acid. The latter melted at 78° and the barium salt was analysed (Found, Ba=39·82; calc., Ba=39·98 per cent.) (Frankland and Duppa, *Annalen*, 1865, **133**, 80; Fittig, *ibid.*, 1877, **188**, 54).

Several attempts were made to increase these yields by variations in the addition of the reagents, but in no case was a yield greater than 60 per cent. obtained. Unless the addition of alkyl haloid and ester is made very slowly, a considerable amount of a by-product, which is probably a butanediol, is formed.

*Preparation of  $\gamma$ -Ethyl-n-hexolactone from Ethyl Succinate.*

Eighty-seven grams of diethyl succinate (b. p. 215—216°) were treated with 30 grams (2·5 mols.) of magnesium powder and 136 grams (2·5 mols.) of ethyl bromide in 400 c.c. of dry ether as described in the preparation of ethyl  $\alpha$ -hydroxy- $\alpha$ -ethylbutyrate. After removal of the ether, an oil was obtained, of which the greater part distilled at 125—140°/23 mm., although a little passed over at 120—123°. The former fraction, weighing 32 grams, was fractionated under the ordinary pressure, when 26 grams distilled at 227—232° (corr.). This fraction was freed from any unchanged ethyl succinate by boiling under reflux with 15 grams of sodium hydroxide for two hours, acidifying with concentrated hydrochloric acid, and boiling for a further half-hour, when an oil separated

on the surface. This was removed and the residue extracted eight times with ether. The oil and ethereal extract were then combined and washed with a little sodium carbonate to remove succinic acid. After removal of the ether, 27 grams of an oil remained, which on redistillation boiled at 229—231° (corr.).

A further 6 grams of the lactone were obtained by working up the fraction distilling at 120—123°/23 mm. The total yield was 33 grams (46 per cent. of the theoretical).

The identity of this compound with  $\gamma$ -ethyl-*n*-hexolactone was established by its conversion into the barium salt of  $\gamma$ -hydroxy- $\gamma$ -ethyl-*n*-hexoic acid (Wischn, *Annalen*, 1867, **143**, 262; Emmert, *Ber.*, 1888, **15**, 1851). The latter was obtained as an amorphous powder, readily soluble in water or alcohol, which on recrystallisation from alcohol gave  $Ba=30.12$  (calc.,  $Ba=30.17$  per cent.).

*Preparation of isoHexolactone from Ethyl Succinate.*

Eighty-seven grams of diethyl succinate were treated with 30 grams (2.5 mols.) of magnesium and 177 grams (2.5 mols.) of methyl iodide exactly as described above. An oil (57 grams: 50 per cent. of the theoretical) was eventually obtained which boiled at 200—202° (Blanc, *Compt. rend.*, 1904, **138**, 579; **139**, 65). The identity of this with *iso*hexolactone was established by conversion into the barium salt of  $\gamma$ -hydroxy*iso*hexoic acid (Found,  $Ba=34.3$ ; calc.,  $Ba=34.3$  per cent.).

Experiments were carried out in which the whole of the ethyl succinate was placed in the flask and the ethyl bromide slowly added, but the reaction was more difficult to control and no greater yield was obtained.

*Action of Magnesium Methyl Iodide on Ethyl Malonate.*

A mixture of 16 grams of ethyl malonate (b. p. 198°) and 36 grams of methyl iodide (2.5 mols.) was added drop by drop to 6 grams of magnesium in 100 c.c. of dry ether as described under the preparation of  $\alpha$ -hydroxy- $\alpha$ -ethylbutyric acid from ethyl oxalate. On decomposing the product with water and dilute sulphuric acid, the greater part of the ethyl malonate was recovered unchanged. From this it would appear that under these conditions ethyl malonate reacts in the enolic form.

*Action of Magnesium Methyl Iodide on Ethyl Ethylmalonate.*

A mixture of 19 grams of ethyl ethylmalonate (b. p. 204—206°) and 36 grams of methyl iodide (2.5 mols.) was added drop by drop

to a well-cooled and stirred mixture of 6 grams of magnesium and 100 c.c. of dry ether as described before. The mixture was allowed to remain overnight at the ordinary temperature and then heated under reflux, on a water-bath, for three hours.

After decomposing, an oil was obtained, the greater part of which distilled at 200—207° and proved to be ethyl ethylmalonate. About 5 grams of a fraction of higher boiling point (220—240°) was collected, and on hydrolysis gave an acid which, when crystallised from light petroleum containing a little acetone, melted at 72°. This acid appeared to be  $\beta$ -hydroxy- $\alpha$ -ethylisovaleric acid, obtained by Grignard (*Compt. rend.*, 1902, **134**, 849) by the action of magnesium methyl iodide on ethyl ethylacetoacetate. The barium salt on analysis gave Ba = 32.07 (calc., Ba = 32.11 per cent.)

*Action of Magnesium Methyl Iodide on Ethyl Dimethylmalonate.*

Slavjanov (*loc. cit.*) obtained  $\beta\delta$ -dihydroxy- $\beta\gamma\delta$ -tetramethylpentane and  $\beta$ -hydroxy- $\alpha\alpha\beta$ -trimethylbutyric acid by heating one equivalent of ethyl dimethylmalonate with three equivalents of magnesium and methyl iodide in the presence of dry ether, on a water-bath for three to five hours.

A mixture of 19 grams of ethyl dimethylmalonate and 36 grams of methyl iodide (2.5 mols.) was added drop by drop to a well-cooled and stirred mixture of 6 grams of magnesium in 100 c.c. of dry ether, as described before. The mixture was allowed to remain overnight at the ordinary temperature, and then heated under reflux on a water-bath for three hours.

After decomposing, an oil separated which on distillation gave a fraction (9 grams) boiling at 190—210° and a second fraction (7 grams) boiling at 220—250°. The former proved to be ethyl dimethylmalonate, whilst the latter, on hydrolysis, gave an acid which on purifying by sublimation melted at 151—152°. This acid appeared to be identical with  $\beta$ -hydroxy- $\alpha\alpha\beta$ -trimethylbutyric acid first prepared by Reformatsky (*Ber.*, 1895, **28**, 2839). During the hydrolysis of the fraction boiling at 220—250° a little insoluble material remained, which on recrystallisation melted at 77°. This was probably  $\beta\delta$ -dihydroxy- $\beta\gamma\delta$ -tetramethylpentane, but there was insufficient material for further examination.

Preliminary experiments on this investigation were carried out at University College, Nottingham, in 1915, under the direction of Prof. Kipping.

The author is indebted to the Research Committee of Messrs.

Nobel's Explosives Co., Ltd., and particularly to Mr. Rintoul, for the facilities accorded him for the completion of this work, and also to Mr. Carr, of Messrs. Boots, Ltd., for permission to publish certain portions of this investigation.

THE RESEARCH LABORATORIES,  
ARDEER.

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### CXI.—*The Melting Points of the Substituted Amides of the Normal Fatty Acids.*

By PHILIP WILFRED ROBERTSON.

OUR knowledge of the physical properties of homologous series is largely due to the researches of Krafft. Whereas the densities approximate to a constant value as the series is ascended, the melting points and boiling points continue to rise, although the successive differences become smaller and smaller. To this general rule, however, the normal fatty acids form a noteworthy exception, since their melting points fall to a minimum and then subsequently rise, and further since the values for the odd and the even members fall on two distinct curves. This exceptional behaviour has been attributed to the association of the earlier members of the series, which itself is probably not unconnected with the arrangement of the atoms in space. Some years ago it was pointed out (Robertson, T., 1908, 93, 1033) that the amides, anilides, and *p*-toluidides showed an even greater irregularity, which was explained, rather vaguely, as being due to molecular dissymmetry. In the hope of obtaining a nearer insight into the relationship between melting point and chemical composition, certain new series, in particular, bromo-derivatives, have now been investigated. In the meantime a systematic search through the earlier and more recent literature had revealed a considerable discrepancy between the values published by different observers; in some cases the melting points given for a compound differed by as much as 20°. In these circumstances it was felt necessary to make a complete redetermination of the melting points of these series. The correctness of a given melting point would appear to depend essentially on the following factors: (a) the identity of the normal fatty acid employed in the preparation, (b) its purity, and especially its freedom from neighbouring homologues, which in the final product can be separated often only with the greatest difficulty; (c) the purity of the product (especially when it is very readily soluble and tends to separate as an oil),

which was attained by numerous recrystallisations from different solvents; (d) the accuracy of the melting point determination. As is indicated in the sequel, every effort has been made to fulfil these conditions.

The melting points of the amides, anilides, *p*-toluidides, *o*-toluidides, *p*-bromoanilides, *o*-bromo-*p*-toluidides, tribromo-anilides,  $\beta$ -naphthylamides, and  $\alpha$ -bromo- $\beta$ -naphthylamides are collected in the following tables. Each series will first of all be considered separately and then the results will be discussed as a whole.

TABLE I.

No. of carbon atoms in chain.		Amides. M. p.		Anilides. M. p.		<i>p</i> -Toluidides. M. p.	
2		82°		112°		153°	
3		77°		106°		126°	
4		115		96		75	
5		106		63		74	
6		101		92		73	
7		96		65		80	
8		105		55		70	
9		99		57		84	
10		99		70		78	
11		90		71		80	
12		100		78		87	
13		100		80		88	
14		103		84		93	
15		—		—		—	
16		106		89		98	
17		—		—		—	
18		109		94		102	

*Amides* (Table I; Fig. 1).

As is clearly visible in the figure, the melting points of the odd and even members fall on two distinct curves, which, although not superposable, rise and fall in the same manner at corresponding places. The initial rise is characteristic only of the amides; the substituted amides, and the fatty acids also, show a fall in melting point at the beginning of the series. It is to be noted that the lower fatty amides, like the corresponding acids, are considerably associated; but the type of melting-point curve is quite different in the two series.

*Anilides* (Table I; Fig. 2).

The melting points of the even anilides fall to a sharp minimum at the eighth member, with a noticeable flattening between the fourth and sixth members. The large fall in melting point between the  $C_6$  and the  $C_8$  anilide, no less than  $37^\circ$ , is very remarkable.



FIG. 1.

*Amides.*

(Even members —; odd members - - - -)

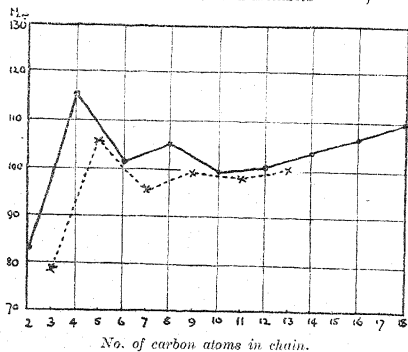
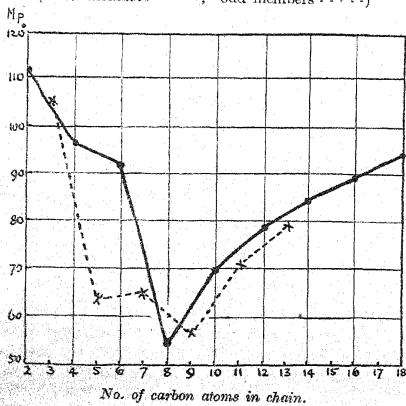


FIG. 2.

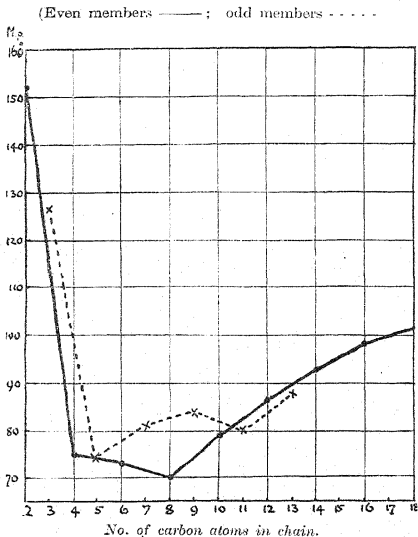
*Anilides.*

(Even members —; odd members - - - -)



The odd series shows a similar large fall followed by a slight rise at the fifth member, corresponding with the flattening in the even series. It is to be noticed that this curve is, at the beginning, exactly the reverse of the odd curve of the amides. The factor causing the irregularity apparently is acting in the reverse sense in

FIG. 3.

*p*-Toluidides.

two series until its effect is eliminated by another factor, some function of the molecular weight, which begins to operate higher in the series.

*p*-Toluidides (Table I; Fig. 3).

The introduction of a methyl group in the para-position of the anilides causes a fundamental change in the melting-point relationships. In the even series the noticeably large initial fall is followed by a very slow decrease to the minimum at the eighth member,

In the odd series, on the other hand, the initial fall is followed by a slight rise and subsequent fall to a second minimum at the eleventh member.

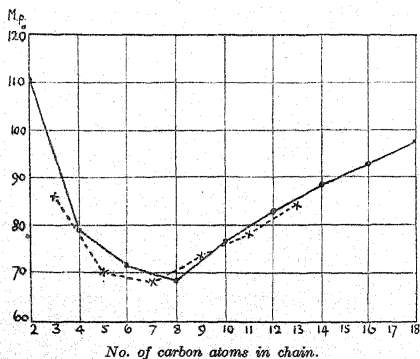
TABLE II.

No. of carbon atoms in chain.		<i>o</i> -Toluidides.	<i>o</i> -Bromo- <i>p</i> -toluidides.	<i>p</i> -Bromo-anilides.
		M. p.	M. p.	M. p.
2		110°	118°	167°
	3	87°	111°	149°
4		79	90	115
	5	70	100	108
6		71	84	105
	7	68	90	98
8		69	78	103
	9	73	86	100
10		78	82	102
	11	78	91	102
12		83	85	104
	13	85	95	—
14		88	89	107
	15	—	—	—
16		—	—	110
	17	—	—	—
18		97	97	114

FIG. 4.

*o*-Toluidides.

(Even members —; odd members - - -)

*o*-Toluidides (Table II; Fig. 4).

Both the odd and even members form the typical curve, that is, the melting points fall to a minimum and then rise again with increasing slowness as the series is ascended.

In Figs. 1 to 4 it is seen that after the eleventh member the melting points of the odd compounds fall slightly below the even values, which behaviour characterises the fatty acids also. This appears to be the general rule, to which the next series is, however, an exception.

*o*-Bromo-*p*-toluidides (Table II; Fig. 5).

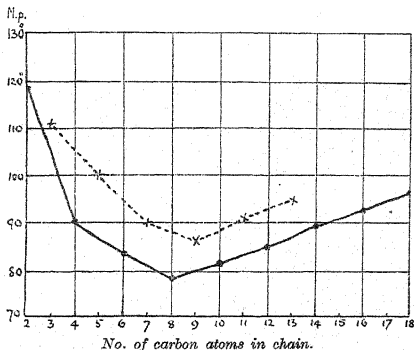
The even and the odd series form typical curves, approximately parallel to each other.

Whereas the odd melting points generally tend to coincide with or fall slightly below the even values, at all events with compounds

FIG. 5.

*o*-Bromo-*p*-toluidides.

(Even members ———; odd members - - - -)



of high molecular weight, here their average melting point is no less than 6° higher. It has not been found possible to correlate this noticeable difference in behaviour with any other characteristic of the series.

*p*-Bromo-anilides (Table II; Fig. 7).

As is seen in Fig. 7, in which the melting points of the even series only are plotted, there is a large fall from the second to the fourth member, followed by a further slow fall to a minimum at the C<sub>10</sub> compound. The odd values fall somewhat below the even and show a minimum at the seventh member.

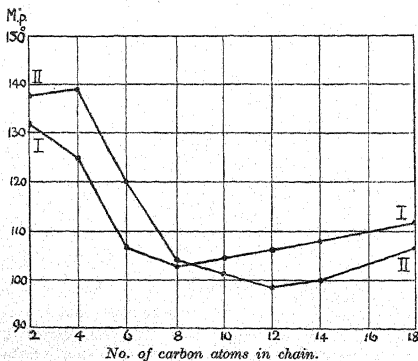
TABLE III.

No. of carbon atoms in chain.		2:4:6-Tri-bromo-anilides. M. p.	$\beta$ -Naphthyl-amides. M. p.	$\alpha$ -Bromo- $\beta$ -naphthylamides. M. p.
2	3	232°	132°	138°
4	5	179	125	139°
6	7	136	107	136
8	9	131	103	111
10	11	129	104	103
12	13	126	106	—
14	15	124	107	99
16	17	124	—	100
18	18	126	112	—

## 2:4:6-Tribromo-anilides (Table III; Fig. 7).

The rapid initial fall in melting point noticed in the *p*-bromo-anilides becomes in this series even more exaggerated, and the minimum is now higher in the series. The curve for the odd members is almost coincident with the even curve.

FIG. 6

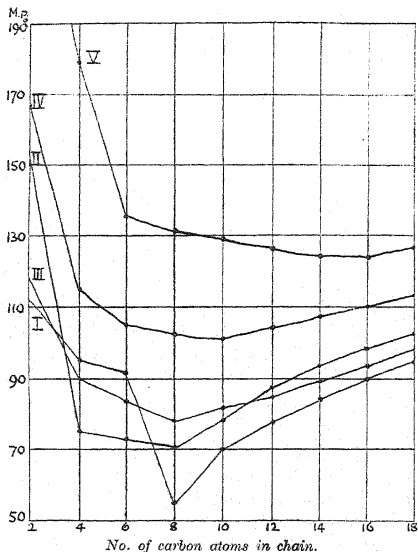


I.  $\beta$ -Naphthylamides. II.  $\alpha$ -Bromo- $\beta$ -naphthylamides.

*$\beta$ -Naphthylamides* (Table III; Fig. 6).

The comparatively slow initial fall in melting point differentiates this series from those hitherto considered. The curve for the odd members at first falls slightly below and then coincides with the even curve.

FIG. 7.



- I. Anilides. II. p-Toluidides. III. o-Bromo-p-toluidides.  
IV. p-Bromo-anilides. V. Tribromo-anilides.

 *$\alpha$ -Bromo- $\beta$ -naphthylamides* (Table III; Fig. 6).

The effect of introducing a bromine atom is to change the initial slow fall in melting point of the  $\beta$ -naphthylamides into a very slight rise, and to cause the minimum to occur higher in the series. The curves for the odd and even members tend to coincide.

*General Discussion.*

From an inspection of Fig. 7, in which several typical curves are collected, it appears that the higher melting-point curves (a) have a

greater initial fall, (b) are flatter in the neighbourhood of the minima, (c) have minima which occur higher up in the series.

If the initial fall in melting point is to be attributed to the greater association of the earlier members, as in the case of the fatty acids, it might be expected to become much less for a series of compounds like the tribromo-anilides, in which the diortho-grouping would prevent molecular association. This initial fall must then be due to some other cause. It should be noticed that it is at all events unconnected with the weight of the substituent radicle. Thus the anilides and *p*-toluidides have totally different types of curve, as likewise the *p*-bromo-anilides and the *o*-bromo-*p*-toluidides.

At a certain distance up the series, in most of the cases examined at about the fourteenth member, the curves tend to become parallel, rising somewhat less rapidly as the weight of the substituent group increases. It would seem then that at this stage the causes of the initial fall in melting point, and the variations in the early part of the curve generally, had been eliminated, and that some single factor, probably the molecular weight, was operative only.

The molecules of a solid may be regarded as being held together in a condition of strain by some force, possibly magnetic (Oxley), on the magnitude of which depend double refraction in particular and the physical properties of the solid generally. The energy of the molecules is almost entirely vibrational, half of which is kinetic and half potential. As the temperature rises the amplitude of vibration of the molecule increases, and when it becomes equal to the mean distance of the molecules apart, which is proportional to the cube root of the molecular volume, the substance melts (Lindemann). Equating the energy in terms of heat required to raise the molecule from the absolute zero to its melting point,  $T_s$ , with the vibrational energy of the molecule at this temperature, one obtains the expression

$$MsT_s = \kappa \cdot MV^{1/3}\nu^2 \quad (\kappa = \text{const.}),$$

where  $M$  is the molecular weight,  $s$  the mean specific heat from the absolute zero to  $T_s$ ,  $V$  the molecular volume, and  $\nu$  the characteristic vibration frequency of the molecule.

It is thus seen that the melting temperature is a function of the specific heat, the molecular volume, and the vibration frequency of the molecule. A suitable variation of these three values would be capable of causing the observed irregularities in the melting points of a series of compounds. This equation also shows that the magnitude of the melting point is independent of any association in the liquid phase, although it is probable that the factors causing

such association would effect the values of  $s$ ,  $V$ , and  $v$  in the sense of increasing the value of  $T_s$ .

High up a series the density and specific heat of successive members become approximately constant, and then

$$T_s = \kappa' \cdot M^{1/2} \quad (\kappa' = \text{const.}).$$

Under such conditions  $v$  is probably some simple function of  $M$ , so that the melting point might be expected to depend on the magnitude of the molecular weight alone. Actually the empirical relation,

$$T_s = \kappa'' \cdot M^{1/2} \quad (\kappa'' = \text{const.}),$$

has been found, with two noticeable exceptions, to give a fair agreement, not only for the higher members of the substituted amides, but for other compounds also (table IV).

TABLE IV.

Compound.	Rise in m. p. for $2\text{CH}_2$ .	
	Experi- mental.*	From formula.
$\text{C}_{18}$ anilide.....	5.0°	4.7°
$\text{C}_{18}$ <i>p</i> -toluidide.....	4.5	4.6
$\text{C}_{18}$ <i>o</i> -toluidide.....	4.5	4.6
$\text{C}_{18}$ <i>p</i> -bromoanilide.....	4.0	4.0
$\text{C}_{18}$ <i>o</i> -bromo- <i>p</i> -toluidide.....	4.0	3.9
$\text{C}_{18}$ $\alpha$ -bromo- $\beta$ -naphthylamide.	3.0	3.2
$\text{C}_{18}$ amide.....	3.0	6.1
$\text{C}_{18}$ $\beta$ -naphthylamide.....	2.0	4.3
Triacotane, $\text{C}_{30}\text{H}_{62}$ .....	3.9	3.6
Montanone, $\text{C}_{55}\text{H}_{110}\text{O}$ .....	1.8	2.2

\* For the substituted amides, the mean difference between the  $\text{C}_{14}$  and  $\text{C}_{18}$  compounds was taken; in the other cases, a slight interpolation was necessary.

# EXPERIMENTAL.

The substituted amides obtained in this investigation were prepared in the following manner. About 1 gram of the fatty acid was mixed in a test-tube with slightly more than the theoretical quantity of thionyl chloride and heated to 100—120° in a sulphuric acid bath for about an hour. The theoretical quantity of base was then added, and the mixture further heated for half an hour to a somewhat higher temperature. The product was recrystallised from alcohol until the melting point was constant, and then finally from light petroleum, with which was mixed, in the case of the less soluble compounds, a small quantity of benzene.

The fatty acids employed were obtained from Kahlbaum. The purity of the solid acids was tested by determining their melting points; the liquid acids were either synthetic or were compared



with Merck's preparations by preparing a common derivative and testing by the method of mixed melting point. The bases were purified by several recrystallisations before being used for the preparations.

Repeated attempts were made to discover the existence of physical isomerides by recrystallising the same compound from different solvents and at different temperatures, and also by having present a trace of alkali or of acid in the solution. All these experiments, however, were without result.

All the melting-point determinations were made by the capillary tube method in a castor-oil bath with the same thermometer, which was compared from time to time with a standard one. When it happened that neighbouring members of a series melted at about the same temperature, their melting points were redetermined simultaneously.

The amides not containing bromine were analysed by the methods of Dumas or Kjeldahl. The bromo-derivatives were analysed by the chromic acid method,\* which with practice enables an estimation to be made in about fifty minutes.

In table V are given the redetermined values of the melting points of the amides, anilides, and *p*-toluidides. The values given by other observers are included for the sake of comparison.

TABLE V.

Compound.	Formula.	M. p.	Previous observers.
<i>n</i> -Valeramide .....	$C_5H_{11}ON$	106°	115° (Weidel); 105° (Fournier); 102° (Hofmann).
<i>n</i> -Hexoamide .....	$C_6H_{13}ON$	101	100° (Hofmann).
<i>n</i> -Heptoamide .....	$C_7H_{15}ON$	96	96° (Hofmann); 95° (Mehlis); 95° (Fournier); 95° (Malherba); 94° (Aschan).
<i>n</i> -Octoamide .....	$C_8H_{17}ON$	105	110° (Fellertar); 106° (Hofmann); 98° (Aschan).
<i>n</i> -Nonoamide .....	$C_9H_{19}ON$	99	99° (Hofmann); 93° (Schalfejew).
<i>n</i> -Decoamide .....	$C_{10}H_{21}ON$	99	108° (Ehestadt); 98° (Hofmann).
<i>n</i> -Undecoamide .....	$C_{11}H_{23}ON$	99	103° (Ehestadt); 81° (Lwow).
Lauramide .....	$C_{12}H_{25}ON$	100	110° (Ehestadt); 102° (Krafft); 99° (Caspari); 97° (Lutz).
<i>n</i> -Tridecoamide .....	$C_{13}H_{27}ON$	100	98° (Lutz).
Myristamide .....	$C_{14}H_{29}ON$	103	102° (Reimer).
Palmitamide .....	$C_{16}H_{33}ON$	106	107° (Krafft); 105° (Hell); 101° (Carlet).
Stearamide .....	$C_{18}H_{37}ON$	109	109° (Krafft); 108° (Hell); 107° (Carlet).
<i>n</i> -Butyranilide .....	$C_{10}H_{13}ON$	96	97° (Beneck); 93° (Fournier); 92° (Kelbe); 90° (Gerhardt); 90° (Autenrieth).

\* Robertson, T., 1915, 107, 902. The following slight modifications have been introduced. Sodium peroxide is used instead of perhydrol, and *N*/20-silver nitrate and thiocyanate in place of *N*/10-solutions.

TABLE V (continued).

Compound.	Formula.	M. p.	Previous observers.
<i>n</i> -Valerianilide .....	C <sub>11</sub> H <sub>15</sub> ON	63°	63° (Fournier); 61° (Easterfield); 60° (Majima).
<i>n</i> -Hexoanilide ... ..	C <sub>12</sub> H <sub>17</sub> ON	92	95° (Kelbe).
<i>n</i> -Heptoanilide .....	C <sub>13</sub> H <sub>19</sub> ON	65	71° (Lwow).
<i>n</i> -Octoanilide .....	C <sub>14</sub> H <sub>21</sub> ON	55	57° (Robertson).
<i>n</i> -Nonoanilide .....	C <sub>15</sub> H <sub>23</sub> ON	57	57° (Robertson).
<i>n</i> -Decoanilide .....	C <sub>16</sub> H <sub>25</sub> ON	70	61° (Robertson).
<i>n</i> -Undecoanilide .....	C <sub>17</sub> H <sub>27</sub> ON	71	68° (Bagard); 64° (Robertson).
Lauranilide .....	C <sub>18</sub> H <sub>29</sub> ON	78	76° (Caspari); 68° (Robertson).
<i>n</i> -Butyro- <i>p</i> -toluidide	C <sub>11</sub> H <sub>15</sub> ON	75	74° (Robertson).
<i>n</i> -Valero- ..	C <sub>12</sub> H <sub>17</sub> ON	74	72° (Robertson).
<i>n</i> -Hexo- ..	C <sub>13</sub> H <sub>19</sub> ON	73	75° (Robertson).
<i>n</i> -Hepto- ..	C <sub>14</sub> H <sub>21</sub> ON	81	80° (Robertson); 79° (Kipping).
<i>n</i> -Octo- ..	C <sub>15</sub> H <sub>23</sub> ON	70	67° (Robertson).
<i>n</i> -Nono- ..	C <sub>16</sub> H <sub>25</sub> ON	84	81° (Robertson).
<i>n</i> -Deco- ..	C <sub>17</sub> H <sub>27</sub> ON	78	80° (Robertson).
<i>n</i> -Undeco- ..	C <sub>18</sub> H <sub>29</sub> ON	80	75° (Bagard); 73° (Robertson).
Lauro- ..	C <sub>19</sub> H <sub>31</sub> ON	87	81° (Robertson).
Myristo- ..	C <sub>21</sub> H <sub>35</sub> ON	93	93° (Robertson).
Palmito- ..	C <sub>23</sub> H <sub>39</sub> ON	98	96° (Robertson).
Stearo- ..	C <sub>27</sub> H <sub>43</sub> ON	102	98° (Robertson).

In table VI are given the new compounds prepared in this investigation, with melting points and analytical results; the percentage values refer to bromine in the case of the bromo-derivatives and to nitrogen for the other compounds.

TABLE VI.

Compound.	Formula.	M. p.	Found per cent.	Calc. per cent.
<i>n</i> -Tridecoanilide .....	C <sub>19</sub> H <sub>31</sub> ON	80°	N=4.7	4.8
<i>n</i> -Trideco- <i>p</i> -toluidide .....	C <sub>20</sub> H <sub>33</sub> ON	88	4.4	4.6
<i>n</i> -Butyro- <i>o</i> -toluidide .....	C <sub>11</sub> H <sub>15</sub> ON	79	8.0	7.8
<i>n</i> -Hexo- ..	C <sub>13</sub> H <sub>19</sub> ON	71	6.6	6.8
<i>n</i> -Hepto- ..	C <sub>14</sub> H <sub>21</sub> ON	68	6.5	6.4
<i>n</i> -Octo- ..	C <sub>15</sub> H <sub>23</sub> ON	69	6.2	6.0
<i>n</i> -Nono- ..	C <sub>16</sub> H <sub>25</sub> ON	73	5.4	5.7
<i>n</i> -Deco- ..	C <sub>17</sub> H <sub>27</sub> ON	76	5.2	5.3
<i>n</i> -Undeco- ..	C <sub>18</sub> H <sub>29</sub> ON	78	5.0	5.0
Lauro- ..	C <sub>19</sub> H <sub>31</sub> ON	83	4.9	4.8
<i>n</i> -Trideco- ..	C <sub>20</sub> H <sub>33</sub> ON	85	4.8	4.6
Myristo- ..	C <sub>21</sub> H <sub>35</sub> ON	88	4.5	4.4
Stearo- ..	C <sub>26</sub> H <sub>43</sub> ON	97	3.8	3.8
<i>n</i> -Butyro- $\beta$ -naphthylamide .....	C <sub>14</sub> H <sub>15</sub> ON	125	6.8	6.6
<i>n</i> -Valero- ..	C <sub>15</sub> H <sub>17</sub> ON	112	6.2	6.2
<i>n</i> -Hexo- ..	C <sub>16</sub> H <sub>19</sub> ON	107	5.6	5.8
<i>n</i> -Hepto- ..	C <sub>17</sub> H <sub>21</sub> ON	101	5.7	5.5
<i>n</i> -Octo- ..	C <sub>18</sub> H <sub>23</sub> ON	103	5.3	5.2
<i>n</i> -Nono- ..	C <sub>19</sub> H <sub>25</sub> ON	103	5.1	4.9
<i>n</i> -Deco- ..	C <sub>20</sub> H <sub>27</sub> ON	104	4.8	4.7
Lauro- ..	C <sub>22</sub> H <sub>31</sub> ON	106	4.4	4.4
<i>n</i> -Trideco- ..	C <sub>23</sub> H <sub>33</sub> ON	107	4.1	4.2
Myristo- ..	C <sub>24</sub> H <sub>35</sub> ON	108	4.1	4.0
Stearo- ..	C <sub>28</sub> H <sub>43</sub> ON	112	3.3	3.4

TABLE VI (continued).

Compound.	Formula.	M. p.	Found per cent.	Calc. per cent.
<i>n</i> -Butyro- <i>p</i> -bromoanilide.....	C <sub>16</sub> H <sub>12</sub> ONBr	115°	Br=33.4	33.1
<i>n</i> -Valero-       ".....	C <sub>17</sub> H <sub>14</sub> ONBr	108	31.3	31.3
<i>n</i> -Hexo-         ".....	C <sub>17</sub> H <sub>16</sub> ONBr	105	30.0	29.6
<i>n</i> -Hepto-        ".....	C <sub>17</sub> H <sub>18</sub> ONBr	98	28.0	28.1
<i>n</i> -Octo-         ".....	C <sub>17</sub> H <sub>20</sub> ONBr	103	26.8	26.9
<i>n</i> -Nono-         ".....	C <sub>15</sub> H <sub>22</sub> ONBr	100	26.0	25.7
<i>n</i> -Deco-         ".....	C <sub>16</sub> H <sub>24</sub> ONBr	102	24.6	24.6
<i>n</i> -Undeco-       ".....	C <sub>17</sub> H <sub>26</sub> ONBr	102	23.7	23.7
Lauro-         ".....	C <sub>18</sub> H <sub>28</sub> ONBr	104	22.3	22.6
Myristo-       ".....	C <sub>20</sub> H <sub>32</sub> ONBr	107	20.8	20.9
Palmito-       ".....	C <sub>22</sub> H <sub>36</sub> ONBr	110	19.8	19.5
Stearo-         ".....	C <sub>24</sub> H <sub>40</sub> ONBr	114	18.4	18.3
Propio- <i>o</i> -bromo- <i>p</i> -toluidide .....	C <sub>10</sub> H <sub>13</sub> ONBr	111	33.4	33.1
<i>n</i> -Butyro-       ".....	C <sub>11</sub> H <sub>14</sub> ONBr	90	30.9	31.3
<i>n</i> -Valero-       ".....	C <sub>12</sub> H <sub>16</sub> ONBr	100	29.5	29.6
<i>n</i> -Hexo-         ".....	C <sub>13</sub> H <sub>18</sub> ONBr	84	28.5	28.1
<i>n</i> -Hepto-        ".....	C <sub>14</sub> H <sub>20</sub> ONBr	90	26.8	26.9
<i>n</i> -Octo-         ".....	C <sub>15</sub> H <sub>22</sub> ONBr	78	25.5	25.7
<i>n</i> -Nono-         ".....	C <sub>16</sub> H <sub>24</sub> ONBr	86	24.7	24.6
<i>n</i> -Deco-         ".....	C <sub>17</sub> H <sub>26</sub> ONBr	82	23.7	23.7
<i>n</i> -Undeco-       ".....	C <sub>18</sub> H <sub>28</sub> ONBr	91	22.3	22.6
Lauro-         ".....	C <sub>19</sub> H <sub>30</sub> ONBr	85	21.3	21.7
<i>n</i> -Trideco-     ".....	C <sub>20</sub> H <sub>32</sub> ONBr	95	21.0	20.9
Myristo-       ".....	C <sub>21</sub> H <sub>34</sub> ONBr	89	20.6	20.3
Stearo-         ".....	C <sub>23</sub> H <sub>40</sub> ONBr	97	17.7	17.7
Propio- <i>α</i> -bromo- <i>β</i> -naphthylamide	C <sub>13</sub> H <sub>13</sub> ONBr	139	29.0	28.8
<i>n</i> -Butyro-       ".....	C <sub>14</sub> H <sub>14</sub> ONBr	139	27.3	27.4
<i>n</i> -Valero-       ".....	C <sub>15</sub> H <sub>16</sub> ONBr	136	25.9	26.2
<i>n</i> -Hexo-         ".....	C <sub>16</sub> H <sub>18</sub> ONBr	120	25.4	25.1
<i>n</i> -Hepto-        ".....	C <sub>17</sub> H <sub>20</sub> ONBr	111	23.9	24.0
<i>n</i> -Octo-         ".....	C <sub>18</sub> H <sub>22</sub> ONBr	104	23.4	23.1
<i>n</i> -Nono-         ".....	C <sub>19</sub> H <sub>24</sub> ONBr	103	22.1	22.1
<i>n</i> -Deco-         ".....	C <sub>20</sub> H <sub>26</sub> ONBr	102	21.7	21.3
Lauro-         ".....	C <sub>22</sub> H <sub>30</sub> ONBr	99	19.5	19.8
Myristo-       ".....	C <sub>24</sub> H <sub>36</sub> ONBr	100	18.6	18.5
Stearo-         ".....	C <sub>26</sub> H <sub>42</sub> ONBr	106	16.4	16.4
<i>n</i> -Butyro-2:4:6-tribromoanilide	C <sub>16</sub> H <sub>10</sub> ONBr <sub>3</sub>	179	58.8	58.3
<i>n</i> -Hexo         ".....	C <sub>17</sub> H <sub>12</sub> ONBr <sub>3</sub>	136	56.3	56.2
<i>n</i> -Hepto-       ".....	C <sub>18</sub> H <sub>14</sub> ONBr <sub>3</sub>	134	54.9	54.4
<i>n</i> -Octo-         ".....	C <sub>19</sub> H <sub>16</sub> ONBr <sub>3</sub>	131	52.8	52.6
<i>n</i> -Nono-         ".....	C <sub>19</sub> H <sub>18</sub> ONBr <sub>3</sub>	131	51.3	51.2
<i>n</i> -Deco-         ".....	C <sub>19</sub> H <sub>20</sub> ONBr <sub>3</sub>	129	49.9	49.7
<i>n</i> -Undeco-       ".....	C <sub>19</sub> H <sub>22</sub> ONBr <sub>3</sub>	129	48.0	48.2
Lauro-         ".....	C <sub>19</sub> H <sub>24</sub> ONBr <sub>3</sub>	126	46.8	46.9
Myristo-       ".....	C <sub>20</sub> H <sub>26</sub> ONBr <sub>3</sub>	124	44.0	44.5
Palmito-       ".....	C <sub>22</sub> H <sub>30</sub> ONBr <sub>3</sub>	124	42.1	42.3
Stearo-         ".....	C <sub>24</sub> H <sub>38</sub> ONBr <sub>3</sub>	126	40.6	40.3

The problem of investigating the relationship between melting point and chemical composition is being extended in other directions to the substituted amides of dibasic and  $\alpha$ -substituted acids. The mathematical interpretation suggested above is from the nature

of things only fragmentary and imperfect, and it has not been possible to suggest a reason why compounds containing the grouping  $\text{CO}\cdot\text{NH}\cdot$  or  $\text{CO}\cdot\text{O}\cdot$  should form series so different in character from other series. The Quantum Theory has not yet been extended to include the investigation of complex molecules, but there is no doubt that a knowledge of the vibration frequency ( $\nu$ ), and the specific heat over a wide range of temperature, is essential for a complete mathematical treatment. The determination of the melting points of a large group of similar compounds is at all events a step in this direction.

My thanks are due to Dr. P. A. Levene for a specimen of tri-decoic acid, and to the Chemical Society for a grant, which has partly defrayed the cost of the investigation.

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## CXII.—*The Effect of Sea-salt on the Pressure of Carbon Dioxide and Alkalinity of Natural Waters.*

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THE total "uncompensated base" or alkali present as carbonate and hydrogen carbonate in sea-water has been determined by Schloësing and Dittmar and by many later investigators. The method used is nearly always titration with standard acid and an indicator of the methyl-orange class, and is subject to the errors of such titrations. The results, expressed in milli-equivalents per litre, are 2.48 (Schloësing) and 2.41 (Dittmar). Moore, Herdman, and the author found values ranging from 2.36 to 2.50 (extreme values), average 2.44, in the water of the Irish sea from November, 1912, to July, 1913 (Herdman, "Report on the Lancashire Sea-Fisheries Scientific Investigations for 1914," *Trans. Biol. Soc. Liverpool*, 1915, 29).

Fox (*Trans. Faraday Soc.*, 1909, 5, 68), by boiling with excess of standard hydrochloric acid and titrating with standard sodium hydroxide and phenolphthalein, found the equivalent of 40 milligrams of hydroxylion on the average, or 2.35 milli-equivalents. The author, in June, 1913, using the same method, found 2.30.

The total carbonic acid may be obtained by boiling with an excess of sulphuric acid in a current of air and absorbing the carbon dioxide in standard barium hydroxide solution. In nearly all cases, however, the alkali of the carbonate and hydrogen carbonate, and hence the total carbon dioxide, has been obtained from the titrations with phenolphthalein and methyl-orange, the difference between these (in equivalents) being numerically equal to the number of molecules of carbonic acid present. The amount of water taken in the work referred to above is 100 c.c., to which five drops of 0.1 per cent. phenolphthalein are added, and the acid ( $N/100$ - or  $N/50$ -hydrochloric acid) is run in until the colour completely disappears. Then five drops of 0.1 per cent. dimethyl-aminoazobenzene or methyl-orange are added, and the titration is continued to a decided reddish-orange. With regard to the phenolphthalein titration, it may be remarked that in fresh water  $N/10$ - down to  $N/1000$ -hydrogen carbonate solutions are still slightly alkaline to phenolphthalein ( $p_H=8.4$  to  $8.2$ ), and the titration should therefore be continued until a weak colour remains. In the case of sea-water, however, the  $p_H$  by extrapolation of the values given later and by direct measurement (see below) is  $7.6$ . This, owing to the presence of salt, will appear to have a  $p_H$  of about  $7.8$ . Consequently, the titration should be continued until the solution is quite colourless. The methyl-orange titrations in dilute solutions, and especially in such as contain salt, are likely to be high. This was verified in the standard carbonate solutions and neutral sea-water, and it was found that from 1 to 2 c.c. of  $N/100$ -hydrochloric acid should be subtracted from the titrations of 100 c.c. Thus the total alkali is probably  $2.24$  to  $2.34$  milli-equivalents per litre. Since the number of c.c. of  $N/100$ -acid required in the phenolphthalein titration is from 1 to 3 for 100 c.c. of water, that is,  $0.1$  to  $0.3$  milli-equivalents per litre, the value of  $R$ =equivalents of alkali÷molecules of carbonic acid is from  $2.3/2.2=1.04$  to  $2.3/2.0=1.15$ . It may be noted that Schlösing found carbonic acid equivalent to  $98.3$  milligrams of carbon dioxide and alkali equivalent to  $99.3$  milligrams of  $SO_3$ , from which  $R=1.12$ .

The alkalinities corresponding with all stages of neutralisation of carbonic acid at different concentrations have already been expressed as general equations (*Proc. Roy. Soc.*, 1915, [4], 91, 535), and those which refer to the dilute solutions contain only the dissociation constants of carbonic acid and the water constant, together with the experimental quantities  $C$ =total concentration of carbonic acid and  $R$  the ratio of alkali to acid. From the curve (*loc. cit.*) connecting  $p_H$  and  $R$ , which agrees well with the

experimental alkalinities of hard water, etc., the following values have been taken in the row of calculated values:

<i>C.</i>	<i>R</i> =	1.06	1.08	1.10	1.12
0.001	<i>p<sub>H</sub></i> =	9.0	9.15	9.25	9.35 (calculated)
0.002	<i>p<sub>H</sub></i> =	8.7	8.9	8.95	8.9 (observed)

Obviously, the alkalinities are much greater than those found in the case of the same carbonate solutions present in sea-water. It seemed desirable to check experimentally this part of the curve in the case of fresh water.

Standard carbonate solutions were prepared by methods independent of indicators and titrations. Some *M*/10-sodium carbonate was made in the usual way. The factor, from the weight of sodium carbonate, was 1.015, by conversion into sodium sulphate 1.016, and by titration, using methyl-orange, 1.018. Some *N*/10-hydrochloric acid made by dilution from a known standard and again analysed by conversion into silver chloride had a factor of 1.000. Mixtures (1), (2), (3), (4) were made from these by adding to 50 c.c. of the *M*/10-sodium carbonate 47.75 c.c., etc., of the hydrochloric acid in order to produce solutions of ratios 1.06, etc., as above. These were kept in tightly corked flasks. So many c.c. were taken as contained the equivalent of 2.2 c.c. of *N*/10-alkali [for example, of mixture (1) 4 c.c.] and made up to 100 c.c. with distilled water free from carbon dioxide. These solutions were all 0.0022*N* with respect to alkali and 0.0021 to 0.00196*M* with respect to carbonic acid. Measured amounts of phenolphthalein were added, and the samples matched against the Sørensen borate-hydrochloric acid standards. The results are given in the third row above. The curve for *C*=0.002 should fall slightly above that calculated for *C*=0.001; actually it is slightly below.

The connexion was then determined between *p<sub>H</sub>* and *R* of sea-water, in which the value of *R* was accurately known. The same standard carbonate solutions were diluted with neutral sea-water instead of with distilled water.

Many experiments carried out with the view of depriving sea-water or sea-salt of its "uncompensated base" and leaving it in a neutral condition were not sufficiently successful to warrant the use of such water in investigating the effect of adding such small quantities of carbonates and hydrogen carbonates. An artificial brine was therefore made from the crystallised salts, which possessed the average composition given in Clarke's "Data of Geochemistry," but omitting the potassium salts and others present in such small amounts that they were likely to have a negligible effect on the

alkalinities. This water was tested for neutrality by means of rosolic acid, which gave a yellow colour quite indistinguishable from that of a standard neutral solution having  $p_H = 7.07$ . The addition of 0.2 c.c. of *N*/100-hydrochloric acid and *N*/100-sodium hydroxide to this water (10 c.c.) produced a perceptible change of colour, showing that the brine contained no appreciable amount of hydrolysed salts or hydrion regulator.

The solutions were then made up from the standard carbonates and this salt water as before. To 10 c.c. were added eight drops of 0.1 per cent. phenolphthalein or six drops of 0.04 per cent.  $\alpha$ -naphtholphthalein. The salt error of the former is about 0.2 in  $p_H$ , and that of the latter is the same to a sufficiently close approximation (Sørensen). The hydrion standards used for comparison were (1) the borate-hydrochloric acid mixtures of Sørensen, (2) the partly neutralised mixture of phosphoric, acetic, and boric acids, which were previously found by the author (*Proc. Roy. Soc.*, 1916, [4], 92, 463) to replace suitably the borate standards from  $p_H = 8.3$  to 8.0. The results are as follows:

$R =$	1.06	1.08	1.10	1.12
$p_H$ found.....	8.1	8.3	8.35	8.3
$p_H$ corrected for salt...	7.9	8.1	8.15	8.1

As in the case of the water without salt, there is practically no change in the alkalinities between  $R = 1.08$  and  $R = 1.12$ .

This was the case also both in the fresh and salt solutions having  $R = 1.16$ .

On the average, then,  $p_H$  is 8.9 in fresh water containing hydrogen carbonate and carbonate of these ratios and carbonic acid at a total concentration of about 0.002 mol., whilst it is 8.1 in salt water, which is identical with respect to alkali and carbonic acid. This effect might, of course, be referred to the less complete primary ionisation of the hydrogen carbonate and carbonate in the presence of so much salt, leading to a diminished hydrolysis. The experimental fact, however, in itself seems to involve biochemical and geochemical consequences, which will be considered after some results on the equilibrium with atmospheric carbon dioxide.

The question whether sea-water is or is not saturated with atmospheric carbon dioxide has been much discussed. Fox (*loc. cit.*) has made a most useful series of observations of the actual pressures of carbon dioxide in equilibrium with waters of varying salinity. The values of hydrion were not then fully available as at present. Obviously there is a relation between hydrion content and pressure of carbon dioxide, and, indeed, from the data

at present available it should be possible to calculate the latter from the values for hydron,  $R$ , etc. There are still, however, difficulties in the way of doing this, except by empirical equations. Some simple experiments carried out in the spring of 1919 at Port Erin throw some light on this question. Pure air, taken from outside the laboratory, was bubbled through sea-water for periods varying from a few hours to twenty-four and twenty-seven. The value of  $p_H$  found in this water was always 8.1.

Numerous blank experiments were being made during this period on the sea-water freshly drawn, and the  $p_H$  values varied between 8.2 and 8.3. This alkalinity was preserved when the water was allowed to remain motionless for a day or more in the laboratory. Thus, the sea-water when exposed to a current of air gained carbon dioxide in every case, and this although the alkalinity was distinctly low for the time of year, since the surface water had been mixed with the lower layers and brought into better contact with the air by recent storms. The usual range in sea-water is from 7.95 to 8.35, but values below  $p_H=8.1$  are exceptional in the case of surface waters, although they have been found in the Skager Rack and off the coast of Norway.

According to the above experiments, all waters of higher alkalinity than  $p_H=8.1$ , that is, nearly all surface waters, will gain carbon dioxide from the air. The experiment was repeated on the artificial sea-water, which was made up with carbonates so that  $p_H$  was 8.2. By saturation with a current of air, this was reduced to 7.9 or 8.1 as measured by different standard solutions and indicators. From the measurements of the neutral sea-water containing known amounts of alkali and carbonic acid, it is seen that  $p_H=8.1$  in salt water corresponds with a ratio of about 1.08, and therefore any sea-water containing less than  $2.2/1.08=2.04$  millimols. of carbonic acid to 2.2 milli-equivalents of alkali should gain carbon dioxide from the air.

This result may be compared with a deduction from Fox's measurements of the absorption of carbon dioxide in salt waters of varying salinity and alkalinity. The "physically dissolved" carbon dioxide is expressed as c.c. of the gas " $a$ " dissolved at different temperatures for each 0.01 per cent. of carbon dioxide in the air. Thus, for his highest salinity=20 per cent. of chlorine, which is nearly equal to that of the artificial salt water of the present work,  $pa=3 \times 0.0875=0.2625$  c.c. per litre of water at  $t=16^\circ$  and  $p_{CO_2}=0.0003$  atmosphere.

The carbon dioxide combined with alkali " $b$ " is given for each milligram of alkali expressed as hydroxyl and for each pressure and temperature of carbon dioxide. At  $t=16^\circ$  and  $p_{CO_2}=0.0003$



atmosphere,  $b$  is 1.18. Taking Fox's value of the total alkali = 40 milligrams of hydroxyl, or 2.35 milli-equivalents, the total carbon dioxide =  $0.26 + (1.18 \times 40)$  c.c.:

$$R = \frac{\text{equivalents alkali}}{\text{mols. of carbonic acid}} = \frac{40 \times 22.4}{17 \times 47.46} = 1.11.$$

If the sea-water has a total alkalinity of 2.2 milli-equivalents, or 37.4 milligrams of hydroxyl,  $R$  becomes 1.05. The value of  $R$  in equilibrium with air is not greatly affected by changes of temperature; thus 1.11 at  $16^\circ$  becomes 1.09 at  $12^\circ$  and 1.115 at  $18^\circ$ .

Thus the direct experimental result is confirmed that, in a water of total alkalinity equal to 2.2 milli-equivalents, the lowest ratio and the highest acidity that is normally encountered in sea-water is only just in equilibrium with atmospheric carbon dioxide, and that in all other cases the water will gain carbon dioxide.

The surface waters of the sea gain carbon dioxide, not only from the air, but also by mixture with the subjacent layers in which low values of  $p_H$  are almost invariably found, and likewise by the decay of plants. It is apparently only the photosynthetic action of seaweeds, plankton, etc., which maintains alkalinities of more than 8.1 in the surface waters. There is no known inorganic chemical agency which is capable of doing this. At the same time, since the pressure of carbon dioxide in the sea becomes greater than that in the atmosphere at alkalinities below  $p_H = 8.1$ , the alkalinity of surface waters cannot fall much below this point.

The alkalinity of bicarbonated fresh waters is also kept at about  $p_H = 8$ , but by a different chemical equilibrium. In these cases, the ratio  $R$ , as defined above, is 1.00, and this, from the curve already quoted, corresponds with  $p_H = 8.2$ . Solutions which have the higher ratios found in sea-water, namely, 1.06 to 1.16, and contain quite an appreciable amount of carbonate, could not long exist in fresh water; they give a strong pink colour with phenolphthalein, as already determined, and would rapidly gain carbon dioxide from the air, and probably also in many cases deposit calcium carbonate or basic magnesium carbonates. The converse effect is best seen by noting the probable course of events when a fresh water of temporary hardness 11, consisting of hydrogen carbonates having the same total alkali concentration as the sea, becomes mixed with it. The static acidity would be greatly raised; thus, if the salt could be added to the original hydrogen carbonate,  $p_H$  would fall to 7.6. This was found by an experiment in which the calculated quantities of the standard carbonate and hydro-

chloric acid were added to the neutral sea-water and the colour given with  $\alpha$ -naphtholphthalein was matched against a "mixed acid" alkali standard. By the mixture of equal volumes of the fresh water and sea-water, the alkalinity would assume an intermediate value, and one lower than that in normal surface waters, whilst the pressure of carbon dioxide would be correspondingly high, and carbon dioxide must be given up to the air or to other large quantities of water until  $R$  rises again to 1.05. It is quite possible that the higher acidities and pressures of carbon dioxide which have been observed everywhere below the surface are due mainly to this cause—the continued addition of bicarbonate waters—without any adequate opportunity of yielding up the excess of carbon dioxide from such immense masses of water. It may also be noted that were it not for the effect of salt in raising to such a high degree the acidity and pressure of carbon dioxide which correspond with a given proportion of alkali and carbon dioxide, the sea would contain much more carbon dioxide than it actually does. Thus, if it consisted of a dilute hydrogen carbonate solution, such as a hard water in equilibrium with the air, it would contain about 5.5 per cent. more carbon dioxide combined with the same quantity of alkali. Since the total carbon dioxide is about 50 c.c. per litre, every cubic metre of sea-water would contain 2.25 litres of carbon dioxide more than at present. The relative availability for plant life of the carbon dioxide in fresh and salt waters is a different question. As shown by Moore and his collaborators (*loc. cit.*), the flora of the sea can use the carbon dioxide of the hydrogen carbonate to a certain limit which approximately corresponds with the production of carbonate. Now, owing to the effect of the salt, sea-water in equilibrium with the air already has a ratio of 1.04 to 1.06; there is some carbonate present. The alkali present in fresh water in equilibrium with the air, and of almost the same alkalinity, is practically all as hydrogen carbonate. Therefore, in the fresh water of the same total alkalinity, for example, 2.2 milli-equivalents per litre, there is more carbon dioxide available before the carbonate point is reached. On the other hand, far more carbon dioxide can be abstracted from sea-water without an excessive rise of alkalinity.

A sea-water of original ratio = 1.06  $\left( = \frac{1}{0.945} \right)$  can, by abstraction of carbon dioxide, have  $R$  changed to 1.16  $\left( = \frac{1}{0.862} \right)$ , losing 8.7 per cent. of the original carbon dioxide, and still only have an alkalinity corresponding with  $p_H = 8.35$ . A fresh water of original ratio = 1.00 can have this changed to  $R = 1.06$  by losing 5.5 per

cent. of the original carbon dioxide, but this changes the alkalinity to the high value corresponding with  $p_H=8.7$ .

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### CXIII.—*The Rate of Hydrolysis of Methyl Acetate by Hydrochloric Acid in Water-Acetone Mixtures.*

By GEORGE JOSEPH BURROWS.

IN a previous paper (T., 1914, 105, 1260) the author recorded some experiments on the inversion of sucrose by acids in water-ethyl alcohol mixtures. It was there found that the rate of inversion at first decreased slightly as water was replaced by alcohol up to about 50 per cent. of alcohol, and then increased. It was concluded from the results that the catalytic activity of the acid was really greater in alcohol than in water, and that the addition of water had a depressing effect on the rate of hydrolysis. At the same time, the author was unable to explain the decrease in the rate of inversion which results from the replacement of water by alcohol up to 50 per cent. mixtures without assuming that the mixed solvents had some specific effect on the rate of reaction, and it was there suggested that this was due to a change in the fluidity of such mixtures, causing a variation in the rate of catalysis similar to that observed in conductivity.

In obtaining the results in that work, the reaction was treated as a unimolecular one, the concentration of the water being neglected. This assumption was made in view of the fact that even in a solution containing 75 per cent. of alcohol by volume the ratio of the number of molecules of water to molecules of sugar present at the commencement of the reaction was 45, so that the decrease in concentration of the water during the reaction was only  $1/45$  of its original value. In a 50 per cent. alcohol mixture the ratio was 91. Under these conditions, it was considered that the concentration of the water could be omitted from the equation and the reaction considered as unimolecular.

If, however, the concentration of the water is considered, the value of  $k_1$ , calculated from the bimolecular equation

$$k_1 = \frac{1}{t(w-b)} \log \frac{b(w-x)}{w(b-x)}$$

(where  $b$  and  $w$  are the number of gram-molecules of sugar and water respectively in the solution at the beginning of the reaction), is, of course, much smaller than the corresponding value of  $k$  obtained from

$$k = \frac{1}{t} \log \frac{b}{b-x}$$

In this case, the total concentration of water is considered to represent its mass as one of the active substances, irrespective of the fact that it is present in large excess and only a small fraction of the total concentration is used up during the reaction.

The difference between the values of  $k$  and  $k_1$  is shown in the following table:

*Sucrose (10 per cent.) and N/2-Hydrochloric Acid at 25.0°.*

Alcohol (volume per cent.).	$k$ .	$k_1$ .
0.0	0.00219	0.0000427
16.7	0.00213	0.0000491
25.0	0.00204	0.0000519
40.0	0.00192	0.0000607
50.0	0.00176	0.0000667
60.0	0.00185	0.0000877
75.0	0.00208	0.0001603

It will be seen that whereas the values of  $k$  pass through a minimum for a certain mixture, the values of  $k_1$  steadily increase.

It appeared of interest to see if similar results would be obtained in the case of ester hydrolysis, and with this end in view experiments have since been performed on the rate of hydrolysis of methyl acetate by hydrochloric acid. Owing to its effect on the equilibrium, alcohol could not be used as one of the solvents in this research, so that the experiments were performed in mixtures of acetone and water. Acetone undergoes change under the influence of the acid used in the hydrolysis, but it has been assumed that this has no effect on the rate of hydrolysis of the methyl acetate.

The acetone used in these experiments was dried over and distilled from calcium chloride. The methyl acetate was freed from acetic acid by means of sodium carbonate and was distilled from calcium chloride; it was neutral to litmus. The volume of the

solution was adjusted at the temperature of the experiment, which was 25° in every case. The acetone percentages given are by volume; thus 70 per cent. acetone was prepared by mixing seven volumes of acetone with three of water. In preparing a 5 per cent. solution of methyl acetate for hydrolysis by  $N/2$ -hydrochloric acid in 70 per cent. acetone, the following method was adopted: 10 c.c. of methyl acetate were diluted to 100 c.c. at 25° with 70 per cent. acetone (*A*), 20 c.c. of 5*N*-hydrochloric acid were mixed with 46.7 c.c. of anhydrous acetone, and the mixture was diluted to 100 c.c. at 25° with 70 per cent. acetone (*B*). Equal volumes of (*A*) and (*B*) were then mixed in a dry flask and placed in a thermostat at 25°. The weights of water and acetone used in preparing the solutions were also determined, so that all concentrations can be expressed in terms of gram-molecular weights. The reaction was followed in the usual way by titrating 5 c.c. of the solution under investigation with baryta solution after different intervals of time, the increase in titre indicating the concentration of the acetic acid produced. At first the reaction was treated as unimolecular, and the values of  $k$  were calculated from the equation

$$k = \frac{1}{t \sqrt{4bn+1}} \log \frac{4bn+2nx(\sqrt{4bn+1}-1)}{4bn-2nx(\sqrt{4bn+1}+1)} \quad (1)$$

obtained by integrating  $\frac{dx}{dt} = k(b-x) - k_2x^2$ .

In this equation  $n = \frac{b-\xi}{\xi^2}$ , where  $\xi$  represents the amount of ester which actually undergoes hydrolysis up to the equilibrium,  $b$  is the initial concentration of ester, and  $x$  the amount hydrolysed in time  $t$ . It was found that the above equation gave values of  $k$  which were quite constant for any particular solution. However, in the case of a series of experiments in different water-acetone mixtures, it was found that as the water was replaced by acetone the value of  $k$  at first decreased and then increased.

Owing to the relatively small concentration of water in solutions containing a high percentage of acetone, it was then decided to calculate all results also from the equation for a bimolecular reaction. The equation used was that given by Griffith and Lewis (T., 1916, 109, 69),

$$k_1 = \frac{1}{tA} \log \frac{A+y+2(K-1)x}{A-y-2(K-1)x} \cdot \frac{A-y}{A+y} \quad (2)$$

obtained by integrating  $\frac{dx}{dt} = k_1(b-x)(w-x) - k_2x^2$ ,

where

$k_1$ =rate of hydrolysis,

$k_2$ =rate of esterification,

$b$ =initial number of gram-molecules of methyl acetate in 1000 c.c. of solution,

$w$ =initial number of gram-molecules of water,

$x$ =number of molecules of ester decomposed in time  $t$ .

In equation (2),

$$y = (w + b)$$

$$A = \sqrt{(w + b)^2 + 4(K - 1)wb}$$

and  $K = \frac{k_2}{k_1} = \frac{C_{\text{ester}} \times C_{\text{water}}}{C_{\text{acetic acid}} \times C_{\text{alcohol}}}$  at equilibrium.

The values of both  $k$  and  $k_1$  obtained in any solution were found to be constant. This is seen in tables I and II, which contain the results for the hydrolysis of 5 per cent. methyl acetate by  $N/2$ -hydrochloric acid in 80 and 90 per cent. acetone (by volume) respectively.

TABLE I.

80 Per cent. Acetone.

$$b = 0.6267; w = 10.20; K = 5.14.$$

$t$ .	$x$ .	$k_1 \times 10^5$ .	$k \times 10^4$ .
0	—	—	—
48.5	0.0506	7.41	7.51
78.5	0.0819	7.44	7.79
111	0.1095	7.43	7.56
138	0.1314	7.34	7.44
168	0.1575	7.44	7.55
228	0.1992	7.32	7.40
258	0.2200	7.36	7.43
318	0.2592	7.47	7.52
401	0.2983	7.31	7.35
$\infty$	0.4963	—	—

Mean ... 7.40 Mean 7.51

TABLE II.

90 Per cent. Acetone.

$$b = 0.6267; w = 4.752; K = 8.97.$$

$t$ .	$x$ .	$k_1 \times 10^5$ .	$k \times 10^4$ .
0	—	—	—
50	0.0636	19.77	9.35
85	0.0991	18.95	8.91
10	0.1262	19.35	9.08
140	0.1523	19.12	8.94
206	0.2018	18.91	8.80
263	0.2435	19.80	9.18
324	0.2695	19.34	8.94
400	0.2957	19.16	8.82
484	0.3192	19.63	9.00
$\infty$	0.3608	—	—

Mean ... 19.56 Mean 9.00

In table III is given a summary of results obtained for the hydrolysis of 5 per cent. methyl acetate by *N*/2-hydrochloric acid in different water-acetone mixtures. The value of  $b$  is 0.6267 in each case. The value of  $K$  was determined by ascertaining at the completion of the reaction the amount of acetic acid produced and then calculating the equilibrium constant. It was found that the numbers so obtained varied with the different solutions. This method of determining the conditions at equilibrium by analysing the solution actually used for the rate of hydrolysis is undoubtedly open to error, as a small amount of the volatile substances must escape each time the flask is opened to determine the concentration of acetic acid at each particular time. The amount lost in this way during a complete experiment would probably be sufficient to introduce an error into the value of  $C$  (acetic acid), and this might lead to quite a large error in the value of  $K$ . The variations in  $K$  are possibly due to a small error in the values of the concentrations of acetic acid found for the various solutions. At the same time, it has been found that a comparatively large difference in  $K$  produces only a small difference in the value of  $k_1$ . Thus the mean value of  $k_1$  for a solution containing 90 per cent. of acetone is found to be 19.56 when  $K=8.97$  and 18.7 when  $K$  is taken as 5, the approximate value found in the other solutions.

In the latter case, however, the numbers obtained for  $k_1$  decrease regularly, whereas if the experimental values of  $K$  are taken there is no such decrease. For this reason, it has been decided to employ the values of  $K$  actually found, although it is realised that the variation in its value for the different solutions may be due, in part at least, to the method of determination.

In the following table, the values under  $k$  are calculated from equation (1), those under  $k_1$  from equation (2).

TABLE III.

*Methyl Acetate (5 per cent.) and N/2-Hydrochloric Acid.*

Acetone (volume per cent.).	Gram-molecules of acetone per litre.	$w$ .	$K$ .	$k_1 \times 10^5$ .	$k \times 10^4$ .
0	0	52.32	5.40	2.76	13.58
20	2.665	42.46	5.10	3.03	12.28
40	5.39	32.08	4.38	3.38	10.33
60	8.10	21.23	4.47	3.86	7.91
70	9.42	15.72	4.51	4.56	7.05
80	10.66	10.20	5.14	7.40	7.51
90	11.84	4.752	8.97	19.56	9.00

It will be seen that the value of  $k_1$  increases regularly as water is replaced by acetone as solvent. The values in the sixth column

under  $k$ , however, at first decrease as water is replaced by acetone and then increase.

A similar result was obtained for the hydrolysis of 2.5 per cent. methyl acetate by  $N/10$ -hydrochloric acid. Owing to the small amount of methyl acetate actually present at equilibrium, the value taken for  $K$  for each of the solutions in this series was the value found in the corresponding solution with 5 per cent. methyl acetate and  $N/2$ -hydrochloric acid.

TABLE IV.

*Methyl Acetate (2.5 per cent.) and  $N/10$ -Hydrochloric Acid.*

In all cases,  $b=0.3133$  gram-molecules per litre.

Acetone. Per cent.	Gram-molecules of acetone.	$w$ .	$k_1 \times 10^6$ .	$k \times 10^4$ .
0	0	54.00	4.78	2.60
20	2.73	43.97	5.40	2.39
40	5.53	33.44	5.76	1.90
60	8.31	22.26	6.40	1.42
70	9.68	16.62	7.42	1.22
80	10.96	10.95	10.23	1.13
90	12.19	5.351	23.60	1.26

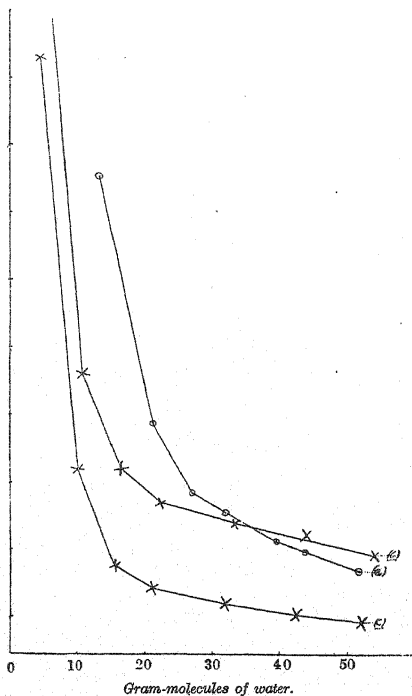
#### *Discussion of Results.*

If the values of  $k_1$  given in tables III and IV are plotted against water concentrations, they are found to lie on a rectangular hyperbola. In the accompanying diagram, a graph is also shown for the results obtained for sucrose inversion given under  $k_1$  in the table at the beginning of this paper. It will be seen that the three curves are similar in shape and indicate the decrease in catalytic activity of the acid which accompanies an increase in the water concentration.

Snethlage (*Zeitsch. physikal. Chem.*, 1913, **85**, 253), Acree (*Amer. Chem. J.*, 1912, **48**, 352), and Taylor (*Zeitsch. Elektrochem.*, 1914, **20**, 201) have advanced the theory that the undissociated molecule of the acid also acts as a catalyst, the activity of the undissociated molecule of hydrochloric acid varying for different reactions up to a value twice that of the hydrogen ion. In order to account for the present results according to this theory, it would be necessary to assume that  $\frac{k_m}{k_H}$  is about 20 ( $k_m$  being the activity of the undissociated molecule and  $k_H$ , that of the hydrogen ion). Figures are not available for the degree of dissociation of hydrochloric acid in water-acetone mixtures, but in discussing the results obtained for the inversion of sucrose (*loc. cit.*), the author



gave values of  $\alpha$  (HCl) deduced for water-alcohol mixtures. In the following table, the values observed for  $k_1$  for sucrose inversion



- (a) Inversion of sucrose in water-alcohol.  
 (b) Hydrolysis of methyl acetate ( $N/10\text{-HCl}$ ) in acetone-water  
 (c) " " " ( $N/2\text{-HCl}$ ) " " "

(calculated as a bimolecular reaction) are compared with the total catalytic activity of the acid expressed as

$$k_m + k_H = k_H[a + 20(1 - a)],$$

the ratio  $\frac{k_m}{k}$  being taken as 20.

TABLE V.

Alcohol (volume per cent.).	$\alpha$ (HCl).	$[\alpha + 20(1-\alpha)]$ .	$k_1 \times 10^5$ .	$\frac{k_1 \times 10^5}{[\alpha + 20(1-\alpha)]}$ .
0	0.86	3.66	4.27	1.17
25	0.83	4.23	5.19	1.23
40	0.80	4.80	6.07	1.26
50	0.72	6.32	6.67	1.06
60	0.65	7.65	8.77	1.15
75	0.45	11.45	16.03	1.11

The numbers in the fifth column approximate to a constant. Although results cannot be calculated in this way for the hydrolysis of methyl acetate in water-acetone mixtures owing to lack of data, it is considered from the results obtained for  $k_1$  in these solutions that if the value of  $\alpha$  (HCl) were available, a similar constancy for  $\frac{k_1}{\alpha + x(1-\alpha)}$  would be obtained for a value of  $x$  in the neighbourhood of 20.

It follows from the above that the activity of the catalyst in these mixtures can best be expressed by  $k_1 = k_m + k_n$ , when the ratio  $\frac{k_m}{k_n}$  is considered to be about 20, but this value is not supported by results obtained by Snethlage and others for the catalytic effect of hydrochloric acid in other reactions.

The shape of the curves in the diagram suggests that in the mixtures investigated the variation of the activity of the acid with the water content is approximately expressed by  $k_1(w+m)=n$ , where  $m$  and  $n$  are constants and  $k_1$  the observed rate of hydrolysis in a solution containing  $w$  gram-molecules of water. An equation of this type is capable of various interpretations, but taken in conjunction with the marked decrease in  $k_1$  with increase in water concentration for low values of the latter, it indicates that the water plays a very markedly anticatalytic rôle compared with the other constituents of the solution, that is, the value of the constant  $m$  must be very small compared with  $w$ . This may be interpreted (compare Lapworth and Fitzgerald, T., 1908, 93, 2168) as being due to the conversion of active, free hydrogen ions to inactive ions by the solvent, the effect of the water in this respect being far greater than that of the acetone. Or it may be interpreted as indicating that the reactive substance in ester hydrolysis is a complex between the ester and water, which is readily dissociated by the excess of water in the solution (Griffiths and Lewis, *loc. cit.*). It may also be interpreted as representing the dissociating effect of the solvent on a complex between the ester and the catalyst, which is considered to be the reactive

substance. Such a complex may either be dissociated by the solvent into the original substances or else hydrolysed by the water into the final products of hydrolysis. For the concentrations usually employed in hydrolysis the amount of this complex is very small owing to the high dissociating power of the water. As the latter is replaced by acetone or other liquid the dissociating power of the medium is decreased and the concentration of the complex is increased, so that the observed rate of hydrolysis is also increased. In any of the above cases it is possible to assign a small value to the term  $m$ , which really represents the relatively small power of the other constituents of the solution of converting an active substance into one which is inactive in catalysis. The following discussion is independent of the nature of  $m$ ; it is concerned rather with its magnitude. We will assume that it is simply a function of the concentration of the other variable in the solution, namely, acetone. If we substitute in the equation  $k_1(w+m)=n$  the values of  $k_1$  and  $w$  in table III for solutions containing (a) 52.32 gram-molecules of water and no acetone, and (b) 4.752 gram-molecules of water and 11.84 of acetone, we obtain the value  $m=0.22$  (in terms of 1 gram-molecule of acetone in the solution). Substituting this value for the other solutions, the following results are obtained.

TABLE VI.

Acetone.	Acetone $\times 0.22$	$w$ .	$k_1 \times 10^5$ .	$n = k_1(w + 0.22 \times \text{acetone})$ .
0.0	—	52.32	2.76	144
2.665	0.59	42.46	3.03	130
5.39	1.19	32.08	3.38	112
8.10	1.78	21.23	3.86	89
9.42	2.07	15.72	4.56	81
10.66	2.35	10.20	7.40	93
11.84	2.60	4.752	19.56	144

The numbers in the last column pass through a minimum value, and vary in a similar manner to the values under  $k$  in table III. Furthermore, for any small value of  $m$  in the equation  $k_1(w+m)=n$ , the values of  $n$  will be found to vary as in table VI. The similarity between the variations of  $k$  in table III and  $n$  in table VI appears to justify the use of the equation for a unimolecular reaction in mixtures such as those used in this work, in which the total concentration of water varies considerably in the different solutions. It would appear that any specific effect of the solvent on the rate of hydrolysis, other than that due to its dissociating power, is more directly shown by disregarding the change in the concentration of the water in the different solutions. It is considered that the minimum value obtained for  $k$  (or  $n$ ) has a definite meaning. It is interpreted as indicating a specific influence of these mixtures on the rate of catalysis, similar to that

observed in the conductivity of certain electrolytes dissolved in them, or in the fluidity of the mixtures themselves. The solution of either alcohol or acetone in water is accompanied by contraction, and it is considered that the condensed state of such a mixture has a retarding influence on catalysis.

### Summary.

The rates of hydrolysis of methyl acetate by *N*/2- and *N*/10-hydrochloric acid have been measured in various water-acetone mixtures. The velocity constants have been calculated according to both unimolecular and bimolecular equations, the reverse reactions being considered in both cases.

It has been found that if the total water concentration is taken as representing its active mass, then the rate of hydrolysis increases as water is decreased in the mixtures throughout the series. The results obtained approximate to  $k_1 = k_m + k_H$  if  $\frac{k_m}{k_H}$  is taken as 20 (approximately). The variation of  $k_1$  with water concentration indicates the anticatalytic function of the latter, and if the values of  $k_1$  are corrected for this effect the numbers so obtained are found to vary in a manner similar to those obtained by using the ordinary unimolecular equation, and pass through a minimum value for a certain mixture. This minimum is considered to have a definite meaning, representing a retarding influence of such mixtures on catalytic reactions.

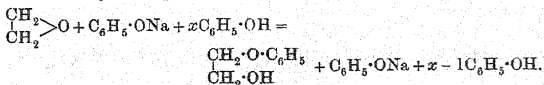
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[Received, August 23rd, 1919.]

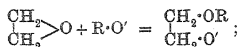
## CXIV.—*The Velocities of Combination of Sodium Derivatives of Phenols with Olefine Oxides.* *Part II.*

By DAVID RUNCIMAN BOYD and MISS DORIS FELTHAM THOMAS.

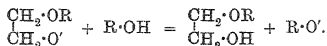
A PREVIOUS communication (Boyd and Marle, T., 1914, 105, 2117) contained an account of experiments on the combination of ethylene and propylene oxides with the sodium derivatives of a variety of phenols. The nature of the reaction investigated is indicated by the equation



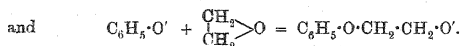
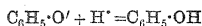
From the results of these experiments, the conclusion was drawn that combination probably, in the first instance, takes place between the phenoxy-ion and the olefine oxide molecule, thus:



the initial additive product afterwards reacting with the excess of phenol to give a glycol aryl ether and a new phenoxy-ion,



A comparison of the values for the velocity constant of the reaction with different phenols indicated that the speed of combination diminished with increase in the acidity of the phenol, and the suggestion was made that a certain analogy exists between the two reactions



In other words, where the tendency for a phenoxy-ion to change into undissociated phenol is great, the speed of combination of the phenoxy-ion with the ethylene oxide molecule should be relatively high, and vice versa. The data available at the time, however, with regard to the relative acidities of different phenols were comparatively few.

An investigation of the extent to which the sodium derivatives of alkyl substituted phenols are hydrolysed in aqueous solution was afterwards carried out by one of us (T., 1915, 107, 1538), and it then became possible to consider in more detail the relationship existing between the acidity of a phenol and the speed with which its sodium derivative combines with ethylene oxide. As a result, certain regularities with regard to the behaviour of ortho-substituted phenols came to light, and it appeared desirable to extend the observations so as to confirm, if possible, the generalisations which had suggested themselves. The present paper therefore includes experimental data for the velocity constants of three additional alkyl substituted phenols, namely, *o*-4-xylenol, *m*-6-xylenol, and mesitol. In all, results for eighteen phenols are dealt with. The facts are summarised in the accompanying diagram, where the velocity constants for the ethylene oxide reaction are plotted against the values for the percentage of hydrolysis of the sodium phenoxides in aqueous solution. A reference to this diagram will show that the velocity constants for phenol and

its meta- and para-substitution products lie approximately along a straight line, whilst the constants for the alkyl substituted phenols containing one alkyl group in an ortho-position lie approximately on a second straight line which runs nearly parallel with the first and some distance below it.

It appears, therefore, that whilst in general the speed of the ethylene oxide reaction increases approximately in proportion to the degree of hydrolysis of the sodium phenoxide, a retarding influence makes itself felt in those cases where an ortho-placed alkyl group is present in the phenol molecule. This retarding influence, it will be observed, is superimposed on the factor which in the main determines the speed of the reaction. It becomes apparent only as the result of such an analysis of the phenomena as is here suggested. A comparison of the actual magnitude of the velocity constant for phenol with that of the constant for any of the alkyl ortho-substituted phenols reveals no such retardation. Thus thymol, in the molecule of which an *isopropyl* radicle is present in the ortho-position to the hydroxyl group, has a velocity constant one and a half times as great as that of phenol. Mesityl, with two ortho-placed methyl groups, has a constant nearly twice as great as that of phenol. None the less, the retarding influence of the ortho-placed alkyl groups is operating in both instances. The case of mesitol is of particular interest in this connexion. Since in mesitol two ortho-placed methyl groups occur, the retardation might be expected to be more pronounced than in cases where only one such group is present. A consideration of the diagram shows that this anticipation is fully borne out by the experimental results.

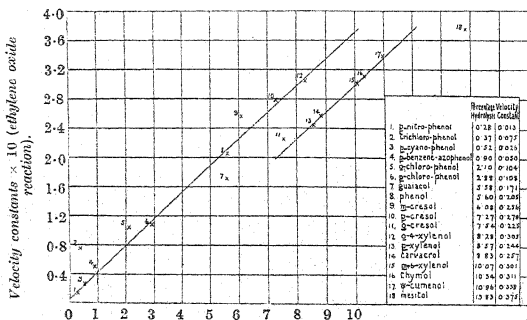
On the other hand, the position of the *o*-chlorophenol constant, and more especially of that for 2:4:6-trichlorophenol, indicates that negative substituents—or at least chlorine atoms—in the ortho-position act in an exactly opposite way, the velocity of combination being accelerated by their presence; and it is noteworthy that just as two ortho-placed alkyl groups cause a very pronounced retardation of the speed, so two ortho-placed chlorine atoms have an accelerating effect much more powerful than that due to a single chlorine atom.

Whilst it is natural to attribute to steric hindrance the retarding influence of the ortho-placed alkyl groups, a final decision on the question is not yet possible in view of the quite different effect produced by ortho-situated chlorine atoms. Further experimental evidence is also required to decide whether the accelerating influence of the chlorine atom should be ascribed to its residual affinity or to its polar quality. In the meantime, it may be pointed out that in the case of guaiacol, which contains an ortho-

situated group of ill-defined polar character, the velocity constant lies some distance above the line for phenols containing ortho-groups of well-marked positive type.

### EXPERIMENTAL.

The velocity constants for *o*-4-xyleneol, *m*-6-xyleneol, and mesitol were determined at 70.4° in 98 per cent. alcohol according to the method previously described (T., 1914, 105, 2117). It was found necessary to employ a mixture of light petroleum with ether (1:1) in separating glycol *m*-6-xyleneol ether from unchanged *m*-6-xyleneol, since this phenol is not completely extracted from an ethereal



Percentage hydrolysis of sodium phenoxides in aqueous solution at 25°.

solution by repeated shaking with aqueous potassium hydroxide. The same method had to be employed in the case of the mesityl ether.

### Summary of Results.

	Percentage yield of glycol ether.			$\frac{1}{t} \log \frac{100}{100-x}$
	2 hours.	1 hour.	Maximum.	
<i>o</i> -4-Xyleneol.	75.3	51.0	98.5	0.3050
	75.1	—	—	—
	75.1	—	—	—
<i>m</i> -6-Xyleneol.	74.5	58.5	98.9	0.3005
	74.8	—	—	—
	74.8	—	—	—
Mesitol.	82.3	—	99.0	0.3745
	81.8	—	—	—
	82.5	—	—	—
	82.5	—	—	—

*Glycol o-xylyl ether*,  $C_8H_9 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$ , is a colourless oil boiling at  $159^\circ/18$  mm. Its *p*-nitrobenzoate crystallises from alcohol in pale yellow plates melting at  $225^\circ$ :

0.1518 gave 6.5 c.c.  $N_2$  (moist) at  $23^\circ$  and 762 mm.  $N=4.82$ .

$C_{17}H_{17}O_5N$  requires  $N=4.62$  per cent

*Glycol m-xylyl ether*,  $C_8H_9 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$ , was obtained as a white solid, which, after recrystallisation from light petroleum, melted at  $57^\circ$ :

0.1621 gave 0.4289  $CO_2$  and 0.1252  $H_2O$ .  $C=72.16$ ;  $H=8.58$ .

$C_{10}H_{14}O_2$  requires  $C=72.23$ ;  $H=8.51$  per cent.

*Glycol mesityl ether*,  $C_9H_{11} \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$ , separates from light petroleum in glistening, white crystals which melt at  $60^\circ$ :

0.1556 gave 0.4196  $CO_2$  and 0.1263  $H_2O$ .  $C=73.54$ ;  $H=9.02$ .

$C_{11}H_{16}O_2$  requires  $C=73.25$ ;  $H=8.97$  per cent.

THE UNIVERSITY COLLEGE  
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## CXV.—Molecular Refractivity of Cinnamic Acid Derivatives.

By ERIC WALKER and THOMAS CAMPBELL JAMES.

THE work of previous investigators has shown that the molecular refractivity of organic compounds is affected to a slight extent by constitutive influences within the molecule. In this investigation we have determined the amount of variation produced by change of constitution in a series of closely allied derivatives of cinnamic acid, and the results are tabulated below:

	$[M]_D$	Difference.	$[M]_D$	Difference.
$\alpha$ -Chlorocinnamic acid .....	50.24	—	50.96	—
$\alpha$ -Chloroallocinnamic acid .....	49.00	1.24	49.59	1.37
Ethyl $\alpha$ -chlorocinnamate .....	58.33	—	58.98	—
Ethyl $\alpha$ -chloroallocinnamate...	57.61	0.72	58.19	0.79
$\alpha$ -Bromocinnamic acid .....	52.90	—	53.52	—
$\alpha$ -Bromoallocinnamic acid .....	52.34	0.56	53.06	0.46
Ethyl $\alpha$ -bromocinnamate .....	60.85	—	61.51	—
Ethyl $\alpha$ -bromoallocinnamate...	60.54	0.31	61.14	0.37
$\beta$ -Bromocinnamic acid .....	51.98	—	52.61	—
$\beta$ -Bromoallocinnamic acid ...	51.53	0.45	52.10	0.51
Dibromocinnamic acid .....	58.94	—	59.64	—
Dibromoallocinnamic acid ...	—	—	—	—
Allyl $\alpha$ -chlorocinnamate.....	62.13	—	62.82	—
Allyl $\alpha$ -chloroallocinnamate ...	60.52	1.61	61.08	1.74



An examination of the above figures confirms Brühl's observation that the more stable isomeride has the higher molecular refractivity, and shows also that, in the  $\alpha$ -substituted compounds, the difference decreases with increase of molecular weight. It is also seen, from a consideration of the bromo-acids, that the  $\alpha$ -substituted acid has a greater refractive power than the  $\beta$ -substituted acid.

## EXPERIMENTAL.

### (a) *Refractivity Measurements.*

*Materials.*—The acids and esters used in this investigation were all specially prepared, and the greatest care was taken to use only highly purified specimens for refractivity measurements. Details of new preparations are given at the end of the paper.

The solvent used for the acids was ethyl alcohol, rendered absolute by distilling the 99.8 per cent. commercial product over lime and afterwards over metallic calcium.

*Apparatus and Method.*—The solutions of the acids were made up by direct weighing to determine their percentage composition. In all cases, approximately 5 per cent. solutions were employed. The esters were all liquids and were determined directly.

Densities were determined by means of a Sprengel-Ostwald pyknometer of about 5 c.c. capacity. The pyknometer was suspended in a thermostat kept at  $25^{\circ}$  ( $\pm 0.05^{\circ}$ ) for about fifteen minutes. The following formula was used:

$$d_{4^{\circ}}^{25^{\circ}} = \frac{WD}{W} - \frac{0.0012(W' - W)}{W},$$

where  $d_{4^{\circ}}^{25^{\circ}}$  = density of solution at  $25^{\circ}$ , referred to water at  $4^{\circ}$ ,

$W'$  = weight of solution filling pyknometer,

$W$  = weight of water filling pyknometer,

$D$  = density of water at  $25^{\circ}$  (0.997073).

Refractive indices were measured by means of a form of Pulfrich refractometer furnished with an ordinary thermostat. The temperature of the liquid in the cell could be maintained at  $25^{\circ}$  ( $\pm 0.05^{\circ}$ ) for a considerable time.

The refractive index of each liquid was measured for the  $C$  and  $D$  lines.

The zero error of the refractometer amounted to  $+1'$ , and all readings were corrected for this. The temperature correction amounted to about one unit in the fifth place of decimals in the refractive index, and could therefore be neglected.

The refractive index of the alcohol used as solvent was deter-



TABLE III.

 *$\alpha$ -Chlorocinnamic Acid.*

Constants for alcohol as in table I.

Solution.	$p$ .	$d$ .	$n_c$ .	$n_D$ .	$r_c$ .	$r_D$ .	$[M]_c$ .	$[M]_D$ .
1a .....	5.190	0.8034	1.36686	1.36893	0.2754	0.2795	50.26	51.01
1b .....	4.984	0.8026	1.36645	1.36851	0.2751	0.2793	50.20	50.97
1c .....	5.136	0.8031	1.36673	1.36879	0.2755	0.2796	50.28	51.03
2a .....	5.469	0.8042	1.36724	1.36930	0.2751	0.2785	50.21	50.83
Means ...							50.24	50.96

TABLE IV.

 *$\alpha$ -Chloroalloccinnamic Acid.*Constants for alcohol:  $d=0.7851$ ;  $n_c=1.35774$ ;  $n_D=1.35954$ .

1a .....	5.008	0.8021	1.36560	1.36758	0.2685	0.2716	49.00	49.57
1b .....	5.051	0.8024	1.36570	1.36767	0.2681	0.2711	48.93	49.48
2a .....	5.206	0.8024	1.36576	1.36776	0.2689	0.2725	49.07	49.73
Means ...							49.00	49.59

TABLE V.

 *$\beta$ -Bromocinnamic Acid.*

Constants for alcohol as in table IV.

1a .....	4.877	0.8062	1.36489	1.36681	0.2296	0.2317	52.12	52.60
2a .....	4.512	0.8045	1.36426	1.36623	0.2284	0.2318	51.85	52.62
Means ...							51.98	52.61

TABLE VI.

 *$\beta$ -Bromoalloccinnamic Acid.*

Constants for alcohol as in table IV.

1a .....	5.044	0.8061	1.36454	1.36649	0.2270	0.2295	51.53	52.10
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TABLE VII.

*Dibromocinnamic Acid.*

Constants for alcohol as in table IV.

1a .....	5.205	0.8107	1.36412	1.36603	0.1926	0.1949	58.94	59.64
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TABLE VIII.

*Ethyl  $\alpha$ -Chlorocinnamate.*

$d$ .	$n_c$ .	$n_D$ .	$r_c$ .	$r_D$ .	$[M]_c$ .	$[M]_D$ .
1.1719	1.56292	1.57054	0.2771	0.2802	58.33	58.98

TABLE IX.

*Ethyl  $\alpha$ -Chloroalloccinnamate.*

1.1569	1.54597	1.55246	0.2737	0.2764	57.61	58.19
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TABLE X.

*Ethyl α-Bromocinnamate.*

<i>d.</i>	<i>n<sub>D</sub></i>	<i>n<sub>D</sub><sup>20</sup></i>	<i>r<sub>c</sub></i>	<i>r<sub>D</sub></i>	[M] <sub>c</sub>	[M] <sub>D</sub>
1.3885	1.57685	1.58450	0.2386	0.2412	60.85	61.51

TABLE XI.

*Ethyl α-Bromoallocinnamate.*

1.3713	1.56474	1.56973	0.2374	0.2398	60.54	61.14
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TABLE XII.

*Allyl α-Chlorocinnamate.*

1.1702	1.56718	1.57483	0.2792	0.2823	62.13	62.82
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TABLE XIII.

*Allyl α-Chloroallocinnamate.*

1.1457	1.53563	1.54164	0.2720	0.2745	60.52	61.08
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*Preparations.*

*Ethyl α-chlorocinnamate*,  $C_6H_5 \cdot CH : CCl \cdot CO_2 \cdot C_2H_5$ .

B. p. 161—162°/8 mm.  $D_4^{25}$  1.172.

0.3467 required 1.621 c.c. *N*-AgNO<sub>3</sub>. Cl=16.60.

$C_{11}H_{11}O_2Cl$  requires Cl=16.84 per cent.

*Ethyl α-chloroallocinnamate.*

B. p. 157—158°/10 mm.  $D_4^{25}$  1.157.

0.2985 required 1.392 c.c. *N*-AgNO<sub>3</sub>. Cl=16.54.

$C_{11}H_{11}O_2Cl$  requires Cl=16.84 per cent.

*Allyl α-chlorocinnamate*,  $C_6H_5 \cdot CH : CCl \cdot CO_2 \cdot CH_2 \cdot CH : CH_2$ .

B. p. 162—163°/11 mm.  $D_4^{25}$  1.170.

0.3340 required 1.470 c.c. *N*-AgNO<sub>3</sub>. Cl=15.61.

$C_{12}H_{11}O_2Cl$  requires Cl=15.93 per cent.

*Allyl α-chloroallocinnamate.*

B. p. 171°/28 mm.  $D^{25}$  1.146.

0.2841 required 1.258 c.c. *N*-AgNO<sub>3</sub>. Cl=15.70.

$C_{12}H_{11}O_2Cl$  requires Cl=15.93 per cent.

From the above, it will be observed that the boiling points and densities of the *allo*-esters are always below those of the *trans*-form.

# CXVI.—*The Determination of Ignition-temperatures by the Soap-bubble Method.*

By ALBERT GREVILLE WHITE and TUDOR WILLIAMS PRICE.

THE soap-bubble method for the determination of ignition-temperatures was first described by McDavid (T., 1917, 111, 1003). In the method as finally adopted, the experimental error is assumed to be less than  $\pm 3^\circ$ , and the results obtained for the ignition-temperatures of the various gases tested are given as:

Coal gas-air .....	878°
Ethylene-air .....	1000
Hydrogen-air .....	747
Carbon monoxide-air .....	931
Petrol (fraction 0—80°)-air .....	995
Benzene-air .....	1062
Ether-air .....	1033

The method is said to eliminate, so far as is practically possible, the time factor. The temperature of ignition is taken to be that temperature to which the gaseous mixture must be heated by the application of a hot body, so as to cause instantaneous ignition. McDavid's results are very high in comparison with other recent determinations.

Finding it necessary to determine the ignition-temperatures of certain ether-air mixtures, the authors decided to use the apparatus described by McDavid on p. 1005 (*loc. cit.*).

The igniting coil was mounted between two binding screws fixed into a small wooden stand, and was kept at the requisite temperature by means of current drawn from a battery of accumulators. A variable resistance of nichrome ribbon formed part of the circuit, which was completed by means of a sliding contact-maker. The current was measured by means of a delicate ammeter reading to 0.01 ampere. The soap solution was prepared by dissolving sodium oleate in water with the addition of a little glycerol. In all the experiments in which ether was used the ether-air mixture was made by weighing the requisite quantity of ether into an exhausted aspirator, from which it was displaced later by means of mercury. It was found that the presence of mercury caused a slight change in the concentration of the solvent above it. The glass pipe from which the bubbles were blown was connected to the aspirator by means of a ground-glass joint, so that there was no possibility of change in the concentration of the ether due to absorption of the vapour by the leading tube, which was of glass. In the other experiments the vapour-air mixture was

made by weighing the requisite amount of liquid into an exhausted 15-litre aspirator, and was in this case displaced by means of water. The hydrogen-air mixture was made up by volume in the same apparatus.

#### *Standardisation of Apparatus.*

The coils were standardised as described by McDavid; the salts used were carefully purified and were kept in an exhausted desiccator over phosphoric oxide. Before use the salt was crushed and only minute fragments were placed on the coil. When these precautions were taken the standardisation could almost invariably be repeated to 0.01 ampere. The number of amperes necessary to keep the coil at such a temperature, that, when in a steady state, the salt was just melted, was taken to be the amperage necessary to heat the coil to the melting point of that salt. The melting points are given in table I, and are the same as given by McDavid, except in the case of lead chloride, which he did not use.

TABLE I.

Salt employed.	Melting point used.	Melting point given in "Chemist's Year Book" for 1916.
Potassium sulphate.....	1072°	1050°
Sodium chloride .....	800	820
Potassium iodide.....	687	705
Lead chloride .....	485	485

For comparison the figures supplied in the "Chemist's Year-Book" for 1916 are given. It will be seen that the difference between these and the figures used is by no means negligible; the figure for lead chloride was taken from this source. Every effort was made to wind the coils as uniformly as possible, but in almost every case it was found that patches rather hotter than the average could be found.

In Fig. 1 are given the standardisations of some of the coils. It will be noticed that these curves are not straight lines, as was that determined by McDavid in the case of the coil used by him, but have a distinct curvature.

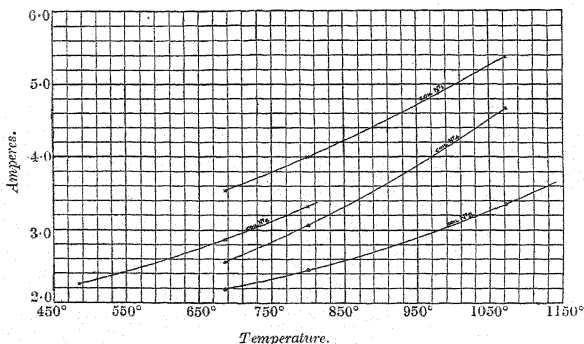
#### *Standardisation of the Method.*

Little work appears to have been done as regards standardising the soap-bubble method. McDavid used a soap-bubble 3.7 cm. in diameter, but no figures are given showing the effect of the size

of the bubble, or the place or the method of striking. All the standardisation undertaken in connexion with this method was done with coil No. 1, and most of it was carried out with ether-air mixtures, although in some cases hydrogen-air mixtures were also used, similar results being obtained. Throughout the work an attempt was made to keep the room temperature within  $2^{\circ}$  of  $18^{\circ}$ . For some time it was found exceedingly difficult to obtain accurate and steady ammeter readings, but the erection of a draught screen round the apparatus, and the gradual elimination of poor connexions, remedied these faults. It was also found that owing to the comparatively high currents used, the nichrome resistance

FIG. 1.

*Showing the standardisation curves connecting the ammeter reading and temperature for various coils.*



required frequent cleaning, and that the sliding contact-maker had to be silvered or fitted with a platinum contact.

So far as could be judged from the steadiness of the ammeter reading, no appreciable change in the temperature of any coil took place when it was brought into contact with a soap bubble blown with air. When using platinum-wound coils at the temperature necessary for the experiments, a very slight draught caused a distinct rise in the ammeter reading.

When determining an ignition-temperature the amperage was taken at which at least two ignitions were obtained out of three attempts, whilst 0.01 ampere below at least three successive failures to ignite were registered.

*Size of Bubble and Place of Striking.*

It was found that the size of the bubble used, and the place of striking, affected the results very appreciably, and various experiments were carried out in order to determine the magnitude of the variations due to these factors. The results of some of these tests are given in table II.

TABLE II.

Position of striking surface on bubble.	Mixture containing 7.5 per cent. of ether in air. Number of amperes necessary to ignite.			Mixture containing 12.5 per cent. of ether in air. Number of amperes necessary to ignite.		
	2.5 cm. bubble.	3.7 cm. bubble.	5 cm. bubble.	2.5 cm. bubble.	3.7 cm. bubble.	5 cm. bubble.
Struck at top .....	5.29	5.05	5.02	5.31	5.20	5.18
Struck at middle ...	5.29	5.05	5.02	5.32	5.20	5.18
Struck at bottom ...	5.41	5.08	5.03	5.43	5.22	5.20

On plotting the above results graphically, as in Fig. 2, it will be seen that the correct result appears to be about 0.01 ampere below the current necessary for the ignition of a 5 cm. bubble. Similar results were obtained using other concentrations of ether vapour in air. It scarcely appears to matter whether the bubble is struck at the top or middle, but striking at the bottom invariably gives a lower result. In practice, bubbles were always struck as near the middle as possible, and a 5 cm. bubble was always used. This size of bubble gave some little trouble owing to a tendency to give delayed ignitions and to burst before use, both effects being particularly noticeable with mixtures containing much ether. There was also a great tendency for the ether to leak through these bubbles. The method of striking was also found to have a great influence on the result, but it was found that a slow, but not too slow, approach of the coil to the bubble, or, even better, of the bubble to the coil, gave very consistent results. When the approach of the bubble was too slow, the ether pouring out through the soap film heated the coil so that the ammeter reading did not register its correct temperature.

*Time between Ignitions.*

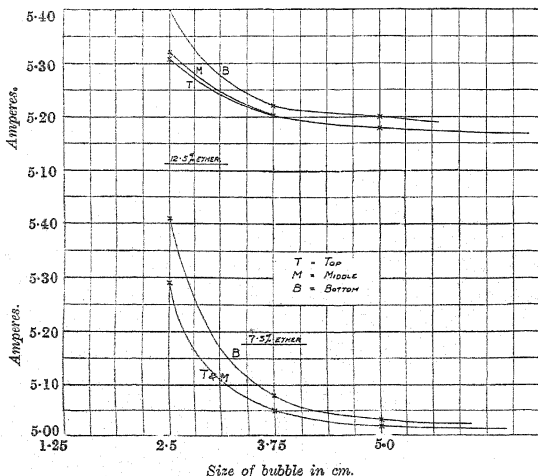
It was also found that a fair time had to elapse after one ignition before another could be attempted with any certainty of obtaining a trustworthy result. Even if a bubble was not ignited, heating of the coil took place, and a second bubble was very often



ignited at what was apparently the same temperature, unless time were given for the coil to cool. At least one minute had to be allowed between each attempted ignition, and often a longer time was necessary, the interval varying from coil to coil. It was also found that the time necessary for an adjustment of temperature

FIG. 2.

*Showing how the current necessary to ignite a definite mixture varies with the size of bubble and position of striking.*



due to change in the magnitude of the current flowing, varied greatly from coil to coil.

#### *Changes in the Coil.*

Even when experiments were carried out precisely as described in the above method, it was found that a coil gave different results for the same combustible mixture, even on the same day. Careful observation showed that these variations were generally all in one direction, and a connexion was soon traced between them and the standardisation of the coil used.

In table III are given the ignition-temperatures of a 4.9 per

cent. ether-air mixture determined with coil No. 1 at various times after standardisation.

TABLE III.

Within 20 minutes.	After 3 days' use.	After 3 weeks' use.	20 Minutes after re-standardising.
968°	985°	1040°	970°

It will be seen at once that the addition of salts to coil No. 1 lowered the ignition-temperature of the ether-air mixture as given by this method by 70°. Some such change might have been anticipated from the later work of Meunier (*Compt. rend.*, 1909, **149**, 924; 1910, **150**, 781). That this was not due to a change in the resistance of the coil can be seen from the fact that throughout the six months during which this coil was in use no point on the standardisation curve varied throughout a range of more than 0.02 ampere except on one occasion, when a variation of 0.03 was found. Precisely similar results were obtained in a test experiment on standardisation, even without washing off the salts used, as was invariably done in practice. A further investigation was then undertaken in order to discover how the ignition-temperature of a particular mixture varied with the treatment to which the coil was subjected.

The ammeter readings taken when using the untreated coil were converted into temperatures after the coil had been standardised by the use of salts. This was considered legitimate as every precaution was taken to ensure that the current-temperature ratio of the coil did not change with use. It was found that the newly-wound coil gave ignition at ammeter readings which increased continuously with time up to a steady value. The first ignition-temperature determined for a 27 per cent. hydrogen-air mixture, using coil No. 2 before treatment, was 760°. In a week's time the ignition-temperature had increased to 860°, but after this time no appreciable change in ammeter reading could be detected.

After standardisation or using salts it was found that a decided rise in the ignition-temperature had always taken place. This was invariably followed by an initially rapid fall, which decreased until a steady state was reached, the rate of decrease of temperature varying considerably with the nature of the coil, and its previous treatment. Thus, an untreated wire would take a very much longer time to reach a steady state than a recently treated or even a well washed wire which had once reached that state. For instance, the ignition-temperature of an ether-air mixture as determined by means of a platinum coil treated for the first time would probably take several days to become constant, whereas in

the case of a recently treated coil twenty minutes would be ample time.

Two hours after coil No. 2 was first treated with salts, the ignition-temperature of a 5 per cent. ether-air mixture as registered by this coil had fallen from  $1068^{\circ}$  to  $1019^{\circ}$ , whilst that of a 12 per cent. mixture, after its preliminary rise from  $986^{\circ}$ , had fallen to  $1006^{\circ}$  (see table IV). In both these cases the ignition-temperature of a 5 per cent. ether-air mixture appears to have fallen much more rapidly than that of a 12 per cent. mixture, as would be expected from the curves shown in Fig. 5.

In order to maintain a coil in the steady state, it was necessary to treat with salts occasionally. This caused a temporary rise in ignition-temperature, but it was only a matter of minutes before the steady state was re-established. The manner in which the ignition-temperature changed when no salts were added to a coil in the steady state can be seen from table III.

The temperature at which a steady state was attained after treatment was greater than without treatment except in the case of coils 1 and 2, which were of platinum. The variation was complicated in the case of the nichrome coil No. 3 by the fact that after being in the steady state for three days with a fairly continuous treatment with salts, a rather rapid fall in ignition-temperature became evident. When the fall became slower, the two points shown by asterisks in Fig. 5 were obtained, the one value, for a 5 per cent. ether-air mixture, being the mean of two readings 0.04 ampere apart obtained before and after the determination for a 12 per cent. ether-air mixture.

It will be noticed that in this case the ignition-temperature of a 5 per cent. ether-air mixture has fallen much more rapidly than that of a 12.5 per cent. mixture. This experiment was unfortunately interrupted by the breaking of the silica tube on which the coil was wound, making it impossible for the experiment to be carried to its logical conclusion; but it is at least possible that a flattened curve well below the original one (without salts) would have been obtained here as in the case of No. 1.

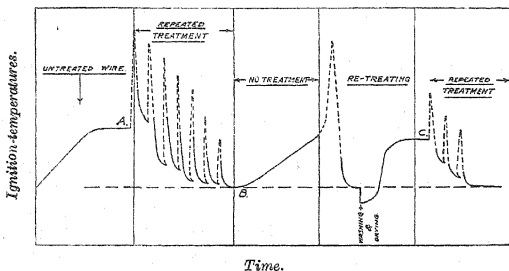
The upward change shown in table III could be made to take place even faster if the salts were washed from the coil and the coil used without treatment after drying. It was found that after eighteen hours' soaking of the coil in water, the ignition-temperature of a 27 per cent. hydrogen-air mixture as indicated by coil No. 1 fell from  $787^{\circ}$  to  $771^{\circ}$  and that of a benzene-air mixture fell from  $1060^{\circ}$  to  $1056^{\circ}$ . After sixty hours' soaking the result obtained for the hydrogen-air mixture was  $773^{\circ}$  and that for the benzene-air mixture  $1056^{\circ}$ . In all the above cases the ignition-

temperature was determined immediately after the drying of the coil was complete. During the course of three days after this preliminary fall, ignition-temperatures determined by this coil continued to rise, and at the end of this time, when the rise had become very slow, the figure found for the hydrogen-air mixture was  $793^{\circ}$  and that for the benzene-air mixture  $1075^{\circ}$ . Further results of a similar kind will be found later.

The effects of the changes considered above are shown in Fig. 3. It will be seen that consistent results are only to be expected under conditions corresponding with the three portions of the curve marked *A*, *B*, and *C*. Except where otherwise stated, results detailed later correspond with these steady states.

FIG. 3.

*Showing diagrammatically the effect of various changes during the treatment of the wire on the ignition-temperatures registered by a coil.*



#### *Influence of the Material of the Coil.*

McDavid (*loc. cit.*) states that the ignition-temperature of a 20 per cent. hydrogen-air mixture as determined by a Eureka wire coil is  $9^{\circ}$  to  $30^{\circ}$  lower than that obtained with platinum wire, and the statement is made that "The figures found by using platinum are higher than those obtained by using Eureka wire, indicating a catalysing effect in the case of the latter. It is, however, probable that both substances exert a catalytic influence." The results given above for coils Nos. 1 and 2 make it certain that the temperatures obtained are influenced very greatly by surface action in every case. It was accordingly decided to determine the ignition-temperatures of various ether-air mixtures using coils of different materials.

*Coil No. 1* was made by winding platinum wire, 0.038 cm. in diameter, round a notched strip of mica.

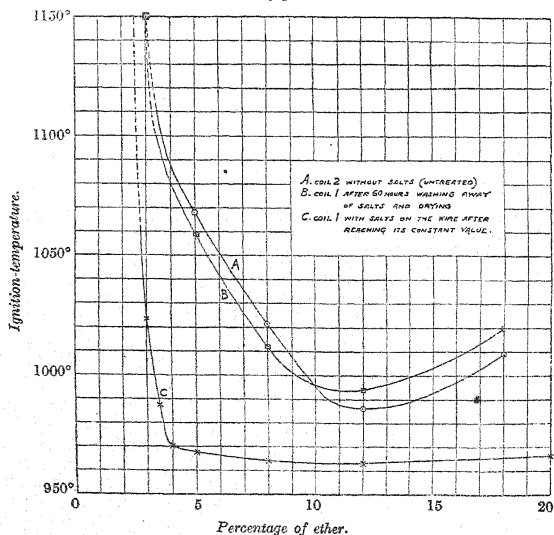
*Coil No. 2* was a similar coil made with platinum wire, 0.025 cm. in diameter.

*Coils Nos. 3 and 4* were made by winding nichrome wire, 0.05 cm. in diameter, round a narrow silica tube.

*Coil No. 5* consisted of platinum wire, 0.025 cm. in diameter,

FIG. 4.

*Showing the ignition-temperatures of various ether-air mixtures obtained with coils of platinum wire wound on mica.*



wound inside a silica tube and having the platinum leads shielded by tubes of silica.

*Coil No. 6* consisted of platinum wire of the same diameter as used in coil No. 5 enclosed in a uniform hard-glass tube with the leads safeguarded as for coil No. 5.

Fig. 4 gives the ignition-temperature curves obtained by plotting the results for various ether-air mixtures determined by means of

coils Nos. 1 and 2. It will be noticed that the curve obtained when coil No. 2 had attained a steady state before being treated with salts (or standardised) is close to that obtained when coil No. 1 had been allowed to attain a steady state after all the salts had been removed by prolonged washing and use. Curve *C* shows the ignition-temperatures obtained when coil No. 1 is treated with salts until the ignition-temperature obtained is constant. It differs from the other two curves inasmuch as the main body is very much flatter and that the difference in ignition-temperature between a 5 per cent. mixture and a 12 per cent. mixture of ether and air is very much less. The ignition-temperature of a 5 per cent. ether mixture as obtained from different curves on this diagram varies by  $100^{\circ}$ , whilst the maximum difference in the case of a 12 per cent. mixture is little more than  $30^{\circ}$ .

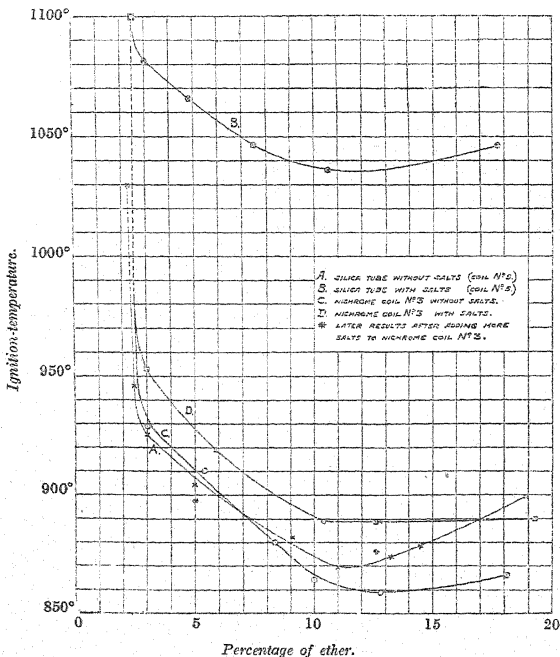
Fig. 5 gives the results obtained, using coils 3 and 5. With both these coils a more or less steady state was attained at a point above the ignition-temperature before treatment, and very much above in the case of the silica tube, No. 5. In this case, as before, the treated coils give flatter curves, and the maximum difference between the ignition-temperatures of 12 per cent. mixtures appears to be about  $175^{\circ}$ , whilst the maximum difference obtained for a 5 per cent. mixture is about  $160^{\circ}$ .

An examination of the results given in these two sets of curves shows that the ignition-temperature of any particular mixture as obtained by this method can vary very greatly. For example, the ignition-temperature of a 12 per cent. mixture of ether and air can be considered to be anything from  $859^{\circ}$  to  $1035^{\circ}$ . The explanation, of course, lies in the fact that a catalytic action—surface action—must be exerted by the coil, as would naturally be expected of any hot body inserted into a combustible gas; but it is fairly evident that the greater catalytic action is not exerted by the coil giving the lower ignition-temperature, as suggested by McDavid, but by that giving the higher. The *modus operandi* is probably as follows: When the coil is brought into the gas the combustible portion near it is at once removed by surface combustion, and this weakens the concentration of combustible gas near the coil to such an extent that it is only when the radiation from the coil is of sufficient intensity to ignite the gas outside this limited sphere that ignition occurs. This reasoning, which appears to be quite in keeping with what is known of the combustion of gases on surfaces, explains why in McDavid's experiments platinum gave a higher result than Eureka wire, and in the experiments described above, why, in the normal state, it gave results higher than either silica or nichrome when unaffected by salts. This

would also explain the reason why a coil had to be used for some time before attaining its maximum activity, as described in the standardisation of the apparatus.

FIG. 5.

*Showing the ignition-temperatures of various ether-air mixtures obtained with coils of nichrome wound on silica and platinum inside silica.*



*Value of Method for obtaining Comparative results.*

Although under any particular set of conditions the soap-bubble method is capable of giving results consistent to within  $\pm 5^\circ$ , it will be seen that, giving as it does, such a range for the ignition-

temperature of any one gas-air mixture, it could scarcely be capable of giving the true ignition-temperature, particularly as surface action is bound to occur even when using the most indifferent material possible. It thus becomes a question as to whether even comparative results could be obtained by this method. It is seen from the curves given in Figs. 4 and 5 that those obtained with different coils occasionally cut one another, indicating that even comparative results could scarcely be obtained, assuming the experimental methods could be guaranteed accurate. As, however, the melting points of the salts used for standardisation purposes are not known to any great degree of accuracy, and the standardisation curves are not straight lines, this evidence can scarcely be regarded as final. It was therefore decided to test several combustible mixtures, using the coils already made, in order to see if comparative results could be obtained by this method. Accordingly, the following mixtures were used, in addition to those mentioned previously:

1. A mixture of 27 per cent. of hydrogen in air.
2. A mixture of 5.7 per cent. of benzene in air
3. A mixture of 0.23 gram of light petroleum (b. p. 90—100°) per litre of air.
4. A mixture of 0.23 gram of light petroleum (b. p. 60—80°) per litre of air.

It was found to be impossible to obtain a definite ignition-temperature for a mixture of carbon disulphide and air or to ignite any mixture of alcohol and air or to obtain a reasonable size of bubble with mixtures of acetone and air. The results obtained are given in table IV.

In the course of these experiments it was noticed that it was easier to obtain an accurate result with hydrogen than with any of the other gases, and it was also very obvious that coils Nos. 5 and 6 gave results sooner and more accurately than the others. With any gases examined, when using these coils, it was easy to redetermine any figure to within 0.01 ampere, whilst with the other coils twice this variation was often found. Coils Nos. 1 and 2 scarcely changed at all during six months' use, but the result was far different in the case of coils wound over silica tubing. For example, three nichrome coils had to be rejected before a coil was found which would not change on heating, and this had to be kept at an exceedingly high temperature for some time before it reached this constant state. To test the comparative accuracy of the method, a second coil of platinum wound inside a hard glass tube was made and the ignition-temperature of a hydrogen-air mixture before treatment with salts determined.



TABLE IV.

Ignition temperature.							
Coil used.		Hydrogen-air, 27 per cent.	Light petroleum (b.p. 90-100°) -air, 0.23 gram per litre.	Light petroleum (b.p. 60-80°) -air, 0.23 gram per litre.	Benzene-air, 5.7 per cent.	Ether-air, 5 per cent.	Ether-air, 12 per cent.
No. 1.	With salts .....	787	1035	1056	1060	968	963
	After washing and use .....	793	1067	1075	1075	1059	994
No. 2.	Without salts .....	860	1038	1040	1045	1068	986
	With salts before constant .....	820	1040	1055	1060	1019	1006
No. 3.	Without salts .....	—	—	—	—	911	859
	With salts .....	—	—	—	—	928	888
No. 4.	Without salts .....	764	1003	999	1025	—	—
	With salts .....	773	1025	1016	1031	—	—
No. 5.	Without salts .....	—	—	—	—	907	870
	With salts .....	—	—	—	—	1064	1035
No. 6.	Without salts .....	715	—	—	—	—	—
	With salts .....	752	—	—	—	—	—
	After washing .....	735	—	—	—	—	—

The result was quite satisfactory, as on standardisation it was found that the ignition-temperature obtained in this case was  $712^{\circ}$ , the result obtained using coil No. 6 being  $715^{\circ}$ . No similar tests were carried out with the other coils, as it was considered that in all cases except that in which a platinum coil was wound inside silica or glass, such a test would probably have been useless, as the ratio of the areas of the two constituent surfaces of the coil was bound to vary for every coil made. The results are interesting, as they show that the ignition-temperatures of two gaseous mixtures obtained by this method may not even be comparative when determined by two different coils. This was carefully tested in the case of the mixtures of the two varieties of light petroleum and air by using coil 4 without salts and coil 1 with salts. When coil No. 4 without salts was kept at  $1001^{\circ}$  and bubbles of the above mixtures were brought into contact with it alternately, in every case the mixture containing the light petroleum of lower boiling point ignited, whilst in only one trial out of five did the other one ignite. A similar experiment with coil No. 2 showed that the ignition-temperature of a mixture containing the light petroleum of lower boiling point was higher than that of the other as measured by this coil.

A similar result was obtained when dealing with a 5 per cent. mixture of ether in air, as in every case except when determined by coil No. 2 before treatment with salts, the ignition-temperature of this mixture was found to be lower than that of the light petroleum and benzene mixtures. In the case of the coil specified, however, the ignition-temperature found for a 5 per cent. mixture of ether in air was definitely higher than those of the other mixtures mentioned above.

In table V are given the maximum and minimum values obtained for the ignition-temperatures of certain of the mixtures used.

TABLE V.

W = Washed.

W.S. = Without salts.

S = After using salts.

Mixture used.	Maximum ignition- temperature observed.	Minimum ignition- temperature observed.	Difference.
Hydrogen (27 per cent.) in air	$860^{\circ}$ Coil 2 W.S.	$715^{\circ}$ Coil 6 W.S.	$145^{\circ}$
Light petroleum (b.p. $90-100^{\circ}$ ) 0.23 gram per litre in air	1067 Coil 1 W.	1003 Coil 4 W.S.	64

TABLE V. (*continued*).

Mixture used.	Maximum ignition- temperature observed.	Minimum ignition- temperature observed.	Difference.
Light petroleum (b.p. 60–80°)	1075°	999°	76°
0.23 gram per litre in air	Coil 1 W.	Coil 4 W.S.	
Benzene (5.7 per cent.) in air	1075	1025	50
	Coil 1 W.	Coil 4 W.S.	
Ether (5 per cent.) in air	1068	907	161
	Coil 2 W.S.	Coil 5 W.S.	
Ether (12 per cent.) in air	1035	859	176
	Coil 5 S.	Coil 3 W.S.	

When it is considered that the glass and silica coils were only used for the hydrogen and ether mixtures respectively, it will be seen that the results have an appreciable regularity as regards what is generally considered to be the catalytic order of the various substances concerned in the ignition. In this connexion, it must not be forgotten that the substance on which a metal coil is wound must affect the ignition-temperature obtained.

A comparison of the ignition-temperatures obtained, using coil No. 2 with and without salts, is also interesting. In the case of the hydrogen-air mixture and the 5 per cent. ether-air mixture, the treated coil gives appreciably lower results than the same coil without salts, but the reverse of this is true of all the other mixtures except light petroleum (b. p. 90–100°) and air when the ignition-temperatures are practically the same in the two cases.

On summing up, it will be seen that the only advantages which the method possesses appear to be those due to its convenience and rapidity in use. It was easy to find the apparent ignition-temperature of any mixture within less than an hour, and, using coils 5 or 6, it could often be done in half that time. The term "instantaneous ignition" is obviously used by McDavid to mean ignition without perceptible delay, but refined methods of time measurement would certainly show that different retardations occurred with different gas mixtures. Its disadvantages appear to lie in the fact that, so far as can be ascertained from these experiments, it cannot give the true ignition-temperature of any gas mixture, and that the results given by it can scarcely be utilised unreservedly even when only required for comparative purposes. Such results are fairly certain to be higher than the true ignition-temperatures, and not, as described by McDavid, lower. The accuracy of the method is also adversely affected by the fact that the exact melting points of the salts used are still a matter for controversy, and that the standardisation curve for any coil appears

from these experiments unlikely to be a straight line. The results are exceedingly dependent on draughts, as the method of estimating temperature is an indirect one. If the temperature of the coil falls during an experiment, due to any such disturbance in outside conditions, the ammeter reading, and hence the temperature indicated, becomes higher instead of lower, owing to the change in resistance of the platinum or other metal forming the heating coil. Any result obtained also seems to depend on the state of the surface causing ignition, as used and unused wire give different ignition-temperatures for the same gas mixture, and an examination under a good lens of wire that has been in use for some time shows it to have altered appreciably in appearance. Amongst its other disadvantages is that of limited applicability. It can only be applied to moist gases and to those which are more or less insoluble in water and can be obtained at a fair concentration in air at the ordinary temperature. For instance, it was found impossible to ignite a mixture of amyl acetate and air, made up at  $20^{\circ}$ , by this method. Another disadvantage lies in the fact that the least concentration of combustible gas at which ignition can be obtained by the soap-bubble method is much greater than that found by ordinary methods, which generally give results below 2 per cent. for ether-air mixtures. Thus the ignition-temperature of any fixed concentration of mixture cannot be determined by this method, as could also be judged from the obvious permeability of the soap film to some of the vapours used.

The results obtained during this investigation appear to indicate that the soap-bubble method of determining ignition-temperatures as described by McDavid gives values for the ignition-temperature which appear to be erroneous. A radical modification of the method could probably be made, however, which would give more satisfactory results. For instance, a soap-bubble of the mixture under examination might be introduced into a vertical tubular furnace, the bubble being shielded from radiation until at the desired spot. In this case, the results would be far more likely to be correct, as the temperature at which ignition took place would be known, and surface action would be partly eliminated.

#### *Summary.*

The soap-bubble method described by McDavid (*loc. cit.*) has been applied to determine the ignition-temperatures of certain mixtures of ether, benzene, light petroleum, and hydrogen with air. The conditions under which consistent results can be obtained are given.

After careful standardisation, the results given by this method were found to be affected by the physical state of the igniting surface and the nature of the material of which it was made; even the addition of small quantities of the salts used for standardisation purposes altered the results obtained. This seemed to show that the method could scarcely give the true ignition-temperature of a gas mixture. The ignition-temperature of a particular gas mixture as determined by two different coils often varied by more than  $150^{\circ}$ , and results appeared to indicate that the method was not strictly trustworthy even for comparative purposes.

In conclusion, the authors desire to express their thanks to Messrs. Nobel's Explosives Co., Ltd., for whom the work was carried out, and to Mr. Wm. Rintoul, Manager of the Research Section, for permission to publish the results, and to Mr. A. W. Sanderson for his kind assistance in carrying out some of the experimental work.

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## CXVII.—*The Interaction of Chlorine and Hydrogen. The Influence of Mass.*

By DAVID LEONARD CHAPMAN and JOHN REGINALD HARVEY  
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AFTER investigating the precautions which must be taken in order to obtain trustworthy actinometric measurements of the velocity of the photochemical action of chlorine and hydrogen, Chapman and Underhill (T., 1913, 103, 496) examined the influence of the concentration of hydrogen on this reaction. The determinations were made with mixtures containing small measured quantities of oxygen, and in the same series of determinations the concentrations of chlorine and oxygen in the mixtures were kept constant, whilst the concentration of hydrogen was varied. They found that "as the partial pressure of the hydrogen is increased from zero, the rate of formation of hydrogen chloride per unit volume of the mixture is at first almost proportional to the concentration of the hydrogen, but the ratio of partial pressure of hydrogen to velocity of interaction rises continuously in value as the propor-

tion of hydrogen is increased, and when the pressure of hydrogen has attained a definite value the rate of formation of hydrogen chloride becomes a maximum, and then, as the proportion of hydrogen is still further increased, the rate of interaction of chlorine and hydrogen falls very slowly."

It had previously been shown by Chapman and MacMahon (T., 1909, 95, 959) that the sensitiveness of electrolytic gas at atmospheric pressure is approximately inversely proportional to the concentration of the oxygen it contains for proportions of oxygen varying between 0.08 and 1 per cent. by volume of the electrolytic gas.

These two results were interpreted by a theory advanced by Burgess and Chapman (T., 1906, 89, 1433).

It was our intention to proceed with the investigation of the influence of the concentration of the chlorine on the rate of formation of hydrogen chloride. However, before we were able to complete our investigation, Bodenstein and Dux (*Zeitsch. physikal. Chem.*, 1913, 85, 297) published the result that the reaction is of the second order in the case of a mixture containing equal volumes of chlorine and hydrogen and a small fixed proportion of oxygen. Our results mentioned above on the influence of the concentrations of hydrogen and oxygen were in the main confirmed by these authors.

It will be remembered that Wildermann (*Phil. Trans.*, 1902, 199, 337) also found that the rate of formation of carbonyl chloride when a mixture containing equal volumes of carbon monoxide and chlorine was exposed to light of constant intensity was proportional to the square of the pressure of the interacting gases.

From Bodenstein and Dux's result and the facts that the rate of interaction is inversely proportional to the concentration of the oxygen and nearly independent of the concentration of the hydrogen (provided that this concentration is not too small), it can obviously be deduced that the rate of formation of hydrogen chloride when a fixed volume of electrolytic gas is exposed to homogeneous light of constant intensity is given approximately by the formula

$$\frac{d[\text{HCl}]}{dt} = \frac{k \cdot I \cdot [\text{Cl}_2]^2}{[\text{O}_2]},$$

in which  $k$  is a constant and  $I$  the intensity of the radiation.

Bodenstein and Dux confirmed the above formula with measurements made with mixtures containing unequal volumes of hydrogen and chlorine.

It may be stated immediately that we are unable to confirm the work of Bodenstein and Dux on the influence of the concen-

tration of the chlorine on the rate of the change. In fact, we find that, within wide limits of concentration of the interacting gases, the rate of formation of hydrogen chloride is given with fairly close approximation by the expression  $\frac{k \cdot I \cdot [\text{Cl}_2]}{[\text{O}_2]}$ , or, in other words, since  $I \cdot [\text{Cl}_2]$  is proportional to the radiation absorbed per second, the hydrogen chloride formed is nearly directly proportional to the radiation absorbed and inversely proportional to the concentration of the oxygen.

The result embodied in the above expression for the rate of formation of hydrogen chloride in mixtures of compositions and pressures within the limits used in our experiments can be easily interpreted by the hypothesis of Chapman, Burgess, Gee, and Underhill. Briefly, the hypothesis in question postulates that the radiation is absorbed by the chlorine molecules. The absorbed energy in the molecules is gradually degraded. In the earlier stages, when the energy is still in a highly efficient form, the degradation is accomplished very rapidly and completely by the agency of oxygen and the other inhibitors. The degradation accomplished in this way is so complete that the resulting degraded energy is no longer capable of assisting the union of the chlorine and hydrogen. The absorbed energy in the chlorine molecules which escapes being degraded in the earlier stages by the inhibitors is transformed to lower forms of energy, which, although capable of activating the chlorine, are to a much less degree, and possibly not at all, degraded by the inhibitors. In other words, the life of an activated molecule is not shortened by the agency of the inhibitors.

Consider unit volume of the mixture of gases exposed to light of intensity  $I$ . The rate of accumulation of efficient energy will be  $k_1 \cdot I \cdot [\text{Cl}_2]$ ,  $k_n$  being now and below taken to represent a constant.

The loss of efficient energy is due to two causes, namely, its degradation during the impacts of the chlorine molecules with oxygen molecules and the conversion of the chlorine molecules into the activated form. When, however, the proportion of oxygen to electrolytic gas is as high as 1 per cent. (as it was in all the experiments to be described below), the sensitiveness is almost one hundred times less than that of the purest electrolytic gas we could prepare, and therefore with such a large proportion of oxygen present, the loss of accumulated efficient energy must be almost entirely due to the first of the above-mentioned causes.

Now the number of impacts per second between chlorine molecules and oxygen molecules is given by the expression

$k_2 \cdot [\text{O}_2][\text{Cl}_2]$ . Further, if it be assumed that in the mean a constant proportion of the efficient energy is degraded during an impact of a chlorine molecule with an oxygen molecule, the degradation of energy during a single impact will be, in the mean,  $k_3\epsilon$ ,  $\epsilon$  being the mean efficient energy of a chlorine molecule after the steady state is reached.

The rate of loss of efficient energy will be the product of the loss during a single impact and the number of impacts per second, which is  $k_2 \cdot k_3 \cdot \epsilon \cdot [\text{O}_2][\text{Cl}_2]$ .

Equating this to the rate of accumulation of efficient energy, we obtain  $k_2 \cdot k_3 \cdot \epsilon \cdot [\text{O}_2][\text{Cl}_2] = k_1 \cdot I \cdot [\text{Cl}_2]$ , and therefore

$$\epsilon = \frac{k_1}{k_2 k_3} \cdot \frac{I}{[\text{O}_2]}.$$

Now if we make the probable assumption that the rate of formation of active chlorine molecules is proportional to the product of the concentration of the chlorine and mean efficient energy of a single molecule,\* the number of active molecules formed per second should be

$$\frac{k_1 \cdot k_4}{k_2 \cdot k_3} \cdot \frac{I \cdot [\text{Cl}_2]}{[\text{O}_2]},$$

but when the pressure of the hydrogen exceeds 15 cm., and possibly at much lower pressures, almost all the active molecules of chlorine combine with hydrogen (Chapman and Underhill, *loc. cit.*), and the rate of formation of hydrogen chloride becomes equal to the active molecules of chlorine produced per second and almost independent of the pressure of the hydrogen.

Therefore the number of molecules of hydrogen chloride formed per second is also given by the expression

$$\frac{k_1 \cdot k_4}{k_2 \cdot k_3} \cdot \frac{I \cdot [\text{Cl}_2]}{[\text{O}_2]}.$$

That is, the hydrogen chloride produced is proportional to the radiation absorbed and inversely proportional to the concentration of the oxygen.

If, as we have reason to believe is the case, hydrogen is a weak inhibitor (Chapman and Underhill, *loc. cit.*), the expression for the rate of formation of hydrogen chloride molecules would become

$$\frac{k_1 \cdot k_4}{k_2 \cdot k_3} \cdot \frac{I \cdot [\text{Cl}_2]}{[\text{O}_2] + k_5[\text{H}_2]}.$$

\* This assumption is equivalent to the assumption that the tendency of each quantum of efficient energy to change its form is independent of the concentration of the chlorine.



in which  $k_5$  is a constant of small magnitude. Since in our experiments, however, the pressures of the hydrogen and the oxygen have been varied in the same ratio, our results are in equal agreement with both formulæ, and fail to distinguish between them.

#### EXPERIMENTAL.

*Experiments with the Moist Gases.*—The apparatus used was a form of Bunsen and Roscoe's actinometer, in which the pressure of the contained gas could be varied, very similar to that used by Chapman and Underhill. The precautions taken in making the measurements and to ensure purity of materials were the same as those observed by Chapman and Underhill.

The mixture of gas experimented with was electrolytic gas which contained about 1.3 per cent. of oxygen by volume. The sensitiveness of the mixture at a pressure of one atmosphere and half an atmosphere was measured, and the results are tabulated below.

Number of experiment.	Sensitiveness at one atmosphere.	Sensitiveness at half an atmosphere.
1.	1000	1029
2.	1000	973
3.	1000	1060

Accordingly, with the moist gases the total hydrogen chloride formed in unit time is almost independent of the pressure, whereas if Bodenstein and Dux's result were correct, the rate of formation of hydrogen chloride ought to be proportional to the pressure.

*Experiments with the Dry Gases.*—For these experiments, the apparatus was modified in one or two respects. The mixture of gases before use was confined in a gas-holder over sulphuric acid. The sulphuric acid which the holder contained was saturated with chlorine and boiled several times, and the gas-holder was so constructed that the sulphuric acid did not come into contact with the air of the laboratory. The actinometer was the same as that used in the experiments with the moist gases, with the exception that the index contained sulphuric acid and the insolation vessel was horizontal and contained anhydrous copper sulphate spread uniformly over the bottom of the tube to serve as an absorbent of the hydrogen chloride. The copper sulphate was carefully dehydrated in the insolation vessel and heated in a current of chlorine at about 300° for an hour. The internal diameter of the insolation vessel was 2.6 cm. The results are tabulated below.

Number of experiment.	Sensitiveness at one atmosphere.	Sensitiveness at half an atmosphere.	Sensitiveness at a quarter of an atmosphere.
1.	1000	963	755*
		936	
2.	1000	—	776*
3.	1000	944	—
4.	1000	—	758*
5.	1000	—	752*

\* At this low pressure it is possible that many of the activated chlorine molecules lose their activity before making fruitful impacts with the hydrogen molecules (compare Chapman and Underhill, *loc. cit.*).

Bodenstein and Dux admit that inhibitors were gradually produced in the insolation vessel during an experiment, and these inhibitors would tend to increase the apparent order of the reaction. They claim to have eliminated the effect of these inhibitors by the method of conducting their experiments, but it seems to us most likely that the discrepancy between their results and ours is due to this cause.

We take this opportunity of gratefully acknowledging a generous grant awarded to one of us by the Board of Scientific and Industrial Research.

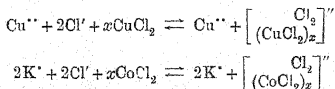
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### CXVIII.—*Auto-complexes in Solutions of Cupric Chloride and Cupric Bromide.*

By STEWART BYRON WATKINS and HENRY GEORGE DENHAM.

IN a paper by Donnan and Bassett (T., 1902, **81**, 939), the view is expressed that the changes in colour brought about in solutions of copper and cobalt salts by changes in concentration and temperature, as well as by the addition of certain other haloid salts, are to be attributed to the formation of complex anions, as exemplified in the following equations:



the colour of the anions so formed differing essentially from the colour of the cupric and cobalt ions. Quantitative support to this theory was first afforded by Kohlschütter's migration experiments (*Ber.*, 1904, **37**, 1193), whilst the investigations of one of the authors (*Zeitsch. physikal. Chem.*, 1909, **65**, 64) have shown that in concentrated aqueous and alcoholic solutions of copper and cobalt haloid salts, the cations have a migration number which is distinctly negative. The present paper is an extension of the investigation, and deals with the effect of temperature and concentration on the migration number of the cupric ion.

The experimental method adopted was practically the same as in the former paper, and the results obtained are of the same order of accuracy. Experiments were nearly always carried out in duplicate, and the middle layer was repeatedly analysed.

Below are the experimental results:

TABLE I.

*Copper Chloride in Aqueous Solution. Temperature, 35°.*

<i>Before electrolysis :</i>	Expt. 1.	2.	3.	4.
Water, grams .....	13.6121	9.1827	7.931	2.1160
Copper, grams .....	0.3455	0.4368	1.0695	0.5273
Concentration in gram-mols per litre .....	0.25	0.75	2.1	4.0
<i>After electrolysis :</i>				
Cathode liquid, grams .....	36.0216	35.4874	41.2016	46.1836
Copper found in cathode liquid, grams .....	0.8176	1.4775	4.2870	7.5189
Voltameter Ag .....	0.2272	0.2718	0.2750	0.1994
Equivalent Cu .....	0.0669	0.0808	0.0810	0.0587
Copper on cathode .....	0.0735	0.0832	0.0252	nil.
Cuprous copper in solution ...	0.0604	0.0784	0.1368	0.1173
Cuprous chloride in solution	0.0941	0.1221	0.2126	0.1828
Cupric copper in solution ...	0.8112	1.3991	4.1702	7.4016
Cupric chloride in solution ...	1.7170	2.9605	8.8256	15.6942
Total salt .....	1.8111	3.0826	9.0382	15.8770
Water .....	34.2105	32.4048	32.1634	30.3066
Migration number .....	0.34	0.24	-0.06	-0.57

*Temperature, 45°.*

<i>Before electrolysis :</i>	Expt. 1.	2.	3.	4.
Water, grams .....	13.6131	9.1827	6.8970	8.1700
Copper, grams .....	0.3455	0.4368	0.9180	1.6600
Concentration in gram-mols. per litre .....	0.25	0.75	2.1	3.2
<i>After electrolysis :</i>				
Cathode liquid, grams .....	32.0180	41.1732	43.9082	48.4132
Copper found in cathode liquid, grams .....	0.6848	1.7113	4.5420	6.8680
Voltameter Ag .....	0.3659	0.3048	0.2611	0.3105
Equivalent Cu .....	0.1052	0.0898	0.0770	0.0915

TABLE I. (*continued*).*Copper Chloride in Aqueous Solution. Temperature, 45°.*

<i>After electrolysis :</i>	Expt. 1.	2.	3.	4.
Copper on cathode .....	0.1161	0.0978	0.0322	nil.
Cuprous copper in solution ...	0.0942	0.0820	0.1217	0.1829
Cuprous chloride in solution	0.1487	0.1277	0.1896	0.2849
Cupric copper in solution.....	0.5906	1.6293	4.4203	6.6851
Cupric chloride in solution ...	1.2500	3.4460	9.3520	14.1500
Total salt .....	1.3967	3.5737	9.5416	14.4349
Water .....	30.6213	37.5995	34.3666	33.9783
Migration number .....	0.22	0.135	-0.01	-0.40

TABLE II.

*Copper Bromide in Aqueous Solution. Temperature, 35°.*

<i>Before electrolysis :</i>	Expt. 1.	2.	3.	4.
Water, grams .....	21.976	6.8659	2.2323	1.2527
Copper, grams .....	0.5036	0.3302	0.2246	0.2847
Concentration in gram-mols. per litre .....	0.36	0.76	1.6	3.6
<i>After electrolysis :</i>				
Cathode liquid, grams .....	42.5353	41.5343	48.6760	57.9704
Copper found in cathode liquid, grams .....	0.8739	1.6396	3.6298	7.3307
Voltameter Ag .....	0.0893	0.1891	0.1857	0.2000
Equivalent Cu .....	0.0272	0.0558	0.0547	0.0589
Copper on cathode .....	0.0394	0.0908	0.0005	nil.
Cuprous copper in solution ...	0.0194	0.0207	0.1089	0.1177
Cuprous bromide in solution	0.0368	0.0467	0.2461	0.2660
Cupric copper in solution.....	0.8590	1.6189	3.5209	7.2130
Cupric bromide in solution ...	3.0200	5.6901	12.3752	25.3589
Total salt .....	3.0568	5.7368	12.6214	25.6249
Water .....	39.4785	35.7973	36.0546	32.3455
Migration number .....	0.32	0.16	0.05	-0.35

*Temperature, 45°.*

<i>Before electrolysis :</i>	Expt. 1.	2.	3.
Water, grams .....	10.7732	2.2323	1.2527
Copper, grams .....	0.2518	0.2246	0.2847
Concentration in gram-mols. per litre .....	0.35	1.6	3.6
<i>After electrolysis :</i>			
Cathode liquid, grams .....	40.8411	40.4290	52.5873
Copper found in cathode liquid, grams .....	0.7959	3.6765	6.6333
Voltameter Ag .....	0.2205	0.1673	0.1937
Equivalent Cu .....	0.0651	0.0489	0.0570
Copper on cathode .....	0.1068	nil	nil
Cuprous copper in solution .....	0.0233	0.0977	0.1140
Cuprous bromide in solution .....	0.0526	0.2206	0.2576
Cupric copper in solution.....	0.7726	3.5788	6.5193
Cupric bromide in solution .....	2.7169	12.5821	22.9200
Total salt .....	2.7695	12.8027	23.1776
Water .....	38.0716	36.6263	29.4061
Migration number .....	0.19	-0.18	-0.88

TABLE III.

*Copper Bromide in Ethyl Alcohol. Temperature, 35°.*

<i>Before electrolysis :</i>	Expt. 1.	2.	3.
Alcohol, grams .....	10.3713	9.0477	5.8932
Copper, grams .....	0.1441	0.2517	0.5059
Concentration in gram-mols. per litre .....	0.21	0.43	1.3
<i>After electrolysis :</i>			
Cathode liquid, grams .....	13.3029	13.7986	16.7181
Copper found in cathode liquid, grams .....	0.1464	0.3244	1.0655
Voltameter Ag .....	0.1124	0.0985	0.1065
Equivalent Cu .....	0.0332	0.0300	0.0314
Copper on cathode .....	0.0151	0.0114	0.0176
Cuprous copper in solution .....	0.0512	0.0466	0.0452
Cuprous bromide in solution .....	0.1156	0.1052	0.1021
Cupric copper in solution .....	0.0952	0.2788	1.0203
Cupric bromide in solution .....	0.3345	0.9767	3.5871
Total salt .....	0.4501	1.0819	3.6892
Alcohol .....	12.8528	12.7167	13.0289
Migration number .....	-0.51	-0.60	-1.1

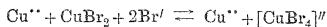
*Temperature, 45°.*

<i>Before electrolysis :</i>	Expt. 1.	2.	3.
Alcohol, grams .....	10.3713	9.0477	5.2739
Copper, grams .....	0.1441	0.2517	0.3822
Concentration in gram-mols. per litre .....	0.21	0.43	1.17
<i>After electrolysis :</i>			
Cathode liquid, grams .....	13.5570	14.0426	15.8708
Copper found in cathode liquid, grams .....	0.1495	0.3282	0.8582
Voltameter Ag .....	0.1033	0.0822	0.1229
Equivalent Cu .....	0.0305	0.0243	0.0362
Copper on cathode .....	0.0098	0.0103	0.0270
Cuprous copper in solution .....	0.0510	0.0382	0.0454
Cuprous bromide in solution .....	0.1152	0.0862	0.1025
Cupric copper in solution .....	0.0985	0.2900	0.8128
Cupric bromide in solution .....	0.3463	1.0038	2.8576
Total salt .....	0.4615	1.0900	2.9601
Alcohol .....	13.0955	12.9526	12.9107
Migration number .....	-0.77	-0.90	-1.35

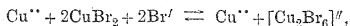
*Discussion of Results.*

The boundary migration experiments described by Steele (*Zeitsch. physikal. Chem.*, 1902, **40**, 689) and by Donnan and Bassett (*loc. cit.*), supported by the quantitative migration experiments of Kohlschütter (*loc. cit.*) and of Denham (*loc. cit.*), have afforded considerable support to the theory of complex-formation in concentrated solutions of copper and cobalt salts. In Denham's experiments it was found that at 25° the migration number of

copper in a 5.29 solution of copper bromide reached the strikingly low value  $-0.39$ . This was interpreted by assuming that in such solutions complex anions of the type  $[\text{CuBr}_4]''$ ,  $[\text{Cu}_2\text{Br}_6]''$ , etc., carried copper out of the cathode compartment. Thus, assuming that the equilibrium



lies almost wholly to the right, the migration number would be approximately zero, whilst if appreciable  $[\text{Cu}_2\text{Br}_6]''$  ions were present, as demanded by the equilibrium



values less than zero would result.

The parallelism between the migration number and the colour of the solution is shown in table IV.

TABLE IV.

*Copper Bromide in Water. Temperature, 25°.*

Concentration.	$u_n$ .	Colour.
0.106	0.445	bluish-green.
0.414	0.440	green.
1.690	0.069	brownish-green.
2.218	0.052	"
3.187	-0.086	brown.
4.055	-0.159	deep brown.
5.288	-0.392	"

On the other hand, many have sought an explanation of this colour-change in the hydration either of the dissolved salt or of the copper cation (notably Biltz, *Zeitsch. physikal. Chem.*, 1902, **40**, 185; Jones and his pupils, *Carnegie Publ.*, No. 60; for complete bibliography, see *Zeitsch. physikal. Chem.*, 1909, **65**, 641). The solution round the cathode may thus become weaker, not only by the wandering away of complex anions containing copper, but by solvent molecules being transported into the cathodic compartment attached to the cation.

That such a transport of solvent molecules attached to ions may occur has been proved by Washburn (*Tech. Quart.*, 1908, **21**, No. 2), although in the cases studied the effect of hydration on migration ratios is not a marked one. Moreover, in their critical review of migration numbers, Noyes and Falk (*J. Amer. Chem. Soc.*, 1911, **33**, 1436) have shown that the true migration number is connected with the apparent or hydrated migration number by the equation

$$T^{\text{Tr}} = T + \Delta N_0 \cdot N / N_0,$$

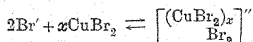
where  $\Delta N_0$  is the number of molecules of water transported to the cathode per faraday;  $N$ =number of equivalents of salt in solution associated with  $N_0$  molecules of solvent;  $T$ =ordinary migration number (referred to solvent, which is assumed stationary);  $T^{Tr}$ =true migration number referred to a non-migrating substance.

If one accepts the hydration value obtained by Jones (*Carnegie Publ.*, No. 60, p. 85), this correction in concentrated solutions is of the order of 5–10 per cent., and therefore negligible in the light of the marked negative values obtained.

The effect of such a "hydration" effect will naturally be the more noticeable in concentrated solutions, but Bein's results (*Zeitsch. physikal. Chem.*, 1898, **27**, 50) for calcium chloride—a salt which, according to Abegg and Bodländer's complex theory (*Zeitsch. anorg. Chem.*, 1899, **20**, 453), should not form complex anions, and, according to Jones (*loc. cit.*), has a strongly hydrated cation—show how small this probable hydration effect is.

Chlorine, per cent.	Tempera- ture.	$n_{Ca}$ .
0.039	22°	0.447
0.42	24	0.405
0.99	21	0.390

Donnan and Bassett's theory postulates that the formation of the complex anion in solutions of copper and cobalt salts is attended by the absorption of heat, that is, it is favoured by a rise of temperature. Thus a solution of cobalt chloride in alcohol, which is blue at the ordinary temperature, becomes pinkish-red on cooling to  $-79^\circ$ . If this is the case, an increase in temperature should bring about a decrease in the migration number due to the equilibrium



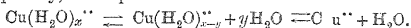
being driven to the right.

On the other hand, the effect of increasing temperature on a hydrated ion will be in all probability to cause a dissociation into a less hydrated or even an anhydrous ion (Lewis, *Zeitsch. physikal. Chem.*, 1905, **52**, 222; 1906, **56**, 223; Biltz, *loc. cit.*; Jones, *loc. cit.*). Jones and West have measured the temperature-coefficients of a large number of salts of varying degree of hydration, and they have concluded that:

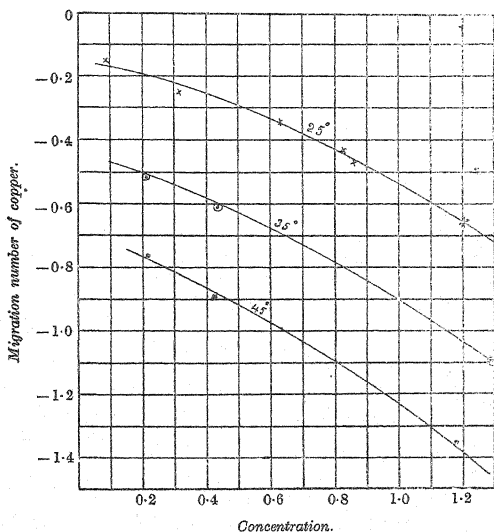
- (1) The temperature-coefficients of aqueous solutions of electrolytes are greater the greater the hydrating power of the electrolyte.

(2) This large increase in conductivity with rise of temperature, in the case of salts forming hydrated ions, is due, in part, to the decreasing complexity of the hydrates formed around the ions.

Consequently, the equilibria



will be driven to the right, and abnormally low migration numbers must consequently tend to approach the normal value (0.4 approx.) with rise of temperature should the abnormality arise from a hydration effect.



In the diagram, the experimental results for copper bromide in alcohol are plotted as a typical example of the definite influence of temperature on the results.

These curves and the tables bring out clearly the rapid decrease in the migration number as the temperature of the solution rises in precise agreement with the demands of the complex theory, in direct contradiction to the demands of Jones' hydration theory.

Moreover, the following results of Bein for salt solutions, wherein



complex formation is scarcely to be expected, bear out the contention that the temperature has very slight influence on the cathodic migration number, even where the evidence of Jones and others indicates that such ions are more or less hydrated.

*Calcium Chloride.*

Chlorine, per cent.	Tempera- ture.	$u_{Ca}$ .
0.42	24°	0.405
0.42	97	0.426
0.77	20	0.395
0.85	94	0.451

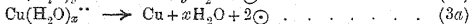
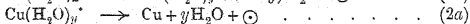
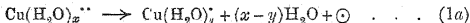
*Lithium Chloride.*

Chlorine, per cent.	Tempera- ture.	$u_{Li}$ .
0.036	20°	0.371
0.036	97	0.389
0.20	25	0.324
0.20	97	0.381

The most convincing evidence of the presence of auto-complexes in the solutions under discussion is, however, afforded by a consideration of the cathodic copper deposit. In a solution of a copper salt, the mechanism of the electrode process may be represented by any one of the three equations:



or, assuming hydration:



(see Foerster and Seidel, *Zeitsch. anorg. Chem.*, 1897, **14**, 106; Foerster and Coffetti, *Zeitsch. Elektrochem.*, 1904, **10**, 736; Bose, *ibid.*, 1898, **5**, 163; Heiberg, *ibid.*, 1903, **9**, 137; Abel, *ibid.*, 1903, **9**, 268; Bodländer and Storbeck, *Zeitsch. anorg. Chem.*, 1897, **14**, 106; Luther, *Zeitsch. physikal. Chem.*, 1900, **34**, 488; 1901, **36**, 385; Wohlwill, Borchers' "Elektrometallurgie," 3rd Ed., p. 198).

Should equation (3) or (3a) represent the cathode process, the ratio  $\frac{\text{weight of copper deposited}}{\text{weight of silver in voltameter}} = 0.295$ , whilst any of the other equations would lead to the value 0.590. Table V shows how

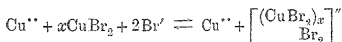
much the experimental values differ from these. In this table, the last column gives the ratio  $\frac{\text{weight of copper deposited}}{\text{weight of silver in voltameter}}$ .

TABLE V.

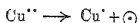
Salt.	Solvent.	Temperature.	Concentration.	$u_{Cu}$ .	$\frac{Cu}{Ag}$ .
$CuBr_2$	water	35°	0.36	0.32	0.44
"	"	35	0.76	0.16	0.48
"	"	35	1.60	0.05	0.002
"	"	35	3.60	-0.35	0.000
"	"	45	0.36	0.19	0.44
"	"	45	1.60	-0.18	0.00
"	"	45	3.60	-0.88	0.000
$CuCl_2$	"	35	0.25	0.34	0.324
"	"	35	0.75	0.24	0.308
"	"	35	2.00	0.181	0.090
"	"	35	4.00	-0.57	0.000
"	"	45	0.25	0.225	0.317
"	"	45	0.75	0.135	0.177
"	"	45	—	0.01	0.123
"	"	45	—	-0.4	0.000
$CuBr_2$	alcohol	35	0.21	-0.51	0.134
"	"	35	0.43	-0.60	0.115
"	"	35	1.30	-1.1	0.165
"	"	45	0.21	-0.77	0.095
"	"	45	0.43	-0.90	0.125
"	"	45	1.17	-1.35	0.219

These figures show that in dilute aqueous solutions much of the current is carried by the discharge of cupric to cuprous ions, and, indeed, actual observation showed that the deposits consisted of a heterogeneous mixture of copper and cuprous haloid salt. In such solutions, the electrode processes included in the equations (1) and (3), or, assuming hydration, (1a) and (3a), prevail, the cuprous ion being immediately precipitated as the insoluble chloride or bromide. The extent to which either process occurs has been shown by Seidel and others (*loc. cit.*) to depend on the variables, temperature, concentration, current density, and concentration of acid, and will in no way be influenced by the presence of hydrated ions in solution, whether those solutions are concentrated or dilute. In many of the more concentrated solutions, however, the ratio  $\frac{Cu}{Ag}$  shows no quantitative agreement with Faraday's laws, whether the reduction to cuprous ion or to copper itself occurs, or both. In a number of experiments, the ratio  $\frac{Cu}{Ag}$  falls to zero, that is, no

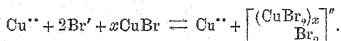
copper or cuprous salt whatsoever is deposited on the cathode. This abnormality, incapable of explanation as it is by the hydration theory, may be satisfactorily explained by the theory of auto-complexes. In concentrated solutions, such equilibria as



are postulated, the undissociated salt, of relatively weak electro-affinity, being forced into a complex anion. As the cuprous ion, however, possesses a more noble potential than does the cupric ion, that is, have a weaker electroaffinity, the cuprous salts, according to Abegg and Bodländer's complex theory (*loc. cit.*), will be more readily forced into a complex than the corresponding cupric salts (Donnan, Abegg's "Handbuch," Kupfer, p. 517). In concentrated solutions, seeing that no metallic copper or copper salt is precipitated on the cathode, the current must be wholly carried in the following way:



(possibly  $\text{Cu}(\text{H}_2\text{O})_x^{++} \longrightarrow \text{Cu}(\text{H}_2\text{O})_y^+ + (x-y)\text{H}_2\text{O} + \odot$ ); the cuprous salt, however, instead of being thrown out of solution, as happens in the more dilute solution, and as demanded by the hydration theory, forms a soluble cupri-cupro-salt with the cupric salt already in solution. It is precisely in those solutions where the absence of deposit on the cathode occurs, that the migration number is so strongly negative. The soluble nature of this cupri-cupro-salt, coupled with the markedly negative migration number, points very strongly to the assumption that such a reaction as the following occurs:



In further confirmation of the views here put forward, a migration experiment was carried out in a U-tube, first with 4*N*-cupric chloride, and secondly with 4*N*-cupric chloride which had been warmed with cuprous chloride, these lower layers being covered by *N*/10-cupric chloride. In both cases, the brown boundary moved towards the anode.

### Summary.

(1) The effect of temperature and concentration on the migration number of solutions (aqueous and alcoholic) of copper bromide and chloride has been investigated.

(2) The effect of increasing temperature and concentration is to cause a marked drop in the migration number of the copper ion, which in concentrated solutions approaches -1 in value.

(3) The formation in concentrated solutions of soluble cupri-cupro-haloid salts at the electrode of the migration vessel has been proved.

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[Received, October 11th, 1919.]

### CXIX.—*Colloidal Electrolytes: Soap Solutions as a Type.*

By JAMES WILLIAM MCBAIN, MARY EVELYN LAING, and  
ALAN FRANCIS TITLEY.

BASED on the extensive data obtained from the study of soap solutions in this laboratory since 1908, McBain and Salmon have defined a new class of compounds, colloidal electrolytes, to which a very large number of substances of great industrial importance may be expected to belong. This comprehensive group is defined as comprising salts in which one ion has been replaced by an ionic micelle of high valency, mobility, conductivity, and degree of solvation. Regarded from another point of view, this means that any colloid which carries electrical charges will in some measure approach the behaviour of a typical colloidal electrolyte. Light is also shed on the properties of colloidal solutions which contain acids, bases, or salts, or to which these have been added. The consistent application of this point of view leads to an ionic micelle theory of all charged colloids; the current assumption that the other charge is carried by the solvent is replaced by the hypothesis that free ions of charge equal and opposite to that of the charged colloid are present in the sol or gel.

Soap was chosen as the subject for investigation, not only because of its industrial importance, but because of its known and definite chemical simplicity and constitution as compared with dyes or protein derivatives, etc. Furthermore, chemical literature contained apparently irreconcilable data obtained by a number of well-known authorities, such as Krafft, Smits, and Kahlenberg. These either assumed that soap was an ordinary neutral colloid, or else, on the contrary, an electrolyte which had suffered extreme hydrolysis with the formation of colloidal residue suspended in a strongly alkaline solution. Each investigator, moreover, considered that the whole problem was solved.

Now it is demonstrated through the measurements of con-

ductivity, osmotic activity, and alkalinity of soap solutions communicated from this laboratory that in concentrated solution the soaps are typical colloidal electrolytes. On dilution, they gradually break down into simple salts. In extreme dilution, acid soaps separate out through hydrolysis. Both catalytic and electromotive force measurements have shown that, except in extreme dilution, hydrolysis is a very minor consideration, the hydroxyl ion being present to the extent of only about  $N/1000$ .

The argument for the existence of the ionic micelle was as follows: In all concentrations the conductivity is high and the osmotic activity, which was measured by the unexceptionable method of dew-point lowering, is only moderate. Hence, in concentrated soap solutions, even if all the osmotic activity is earmarked for the potassium, sodium, or ammonium ion, nearly or quite half of the conductivity remains to be accounted for. This conductivity must evidently be ascribed to some constituent that does not exert appreciable osmotic pressure and that therefore must be colloidal. One of us (J.W.M., *Trans. Faraday Soc.*, 1913; 9, 99; *Kolloid Zeitsch.*, 1913, 12, 256) has shown how this is possible and probable by applying the principle of Stokes's law to the hypothesis of a heavily charged, heavily hydrated ionic micelle which would exhibit excellent conductivity and high viscosity at the same time.

Although our investigation of soap solutions has only reached its first stage, it has been possible on the basis of the above reasoning to set up a comprehensive theory which explains and reconciles all the mass of data of the most diverse sort which has already been accumulated. The various details of this theory, beyond the rough outline given above, will be mentioned and discussed in turn as we come to the new and confirmatory experimental evidence described below.

This communication presents measurements of the freezing point and conductivity of nearly all the soap solutions which can be studied at 0°. Such comprise solutions of the potassium salts of the saturated fatty acids up to and including the laurate ( $C_{12}$ ) in all concentrations, and of the sodium salts up to the octoate ( $C_8$ ). Further, the values for potassium oleate can be measured up to 0.6*N* (0.8*N* is a solid jelly at the ordinary temperature), and sodium oleate up to 0.4*N*, a solution which is already quite viscous.\* All other sodium, potassium, and ammonium soaps

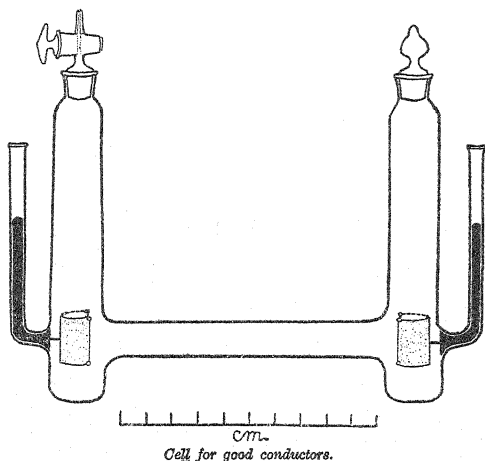
\* The stable form of the sodium oleate solutions at 18° is a white curd. The conductivity at 18° of a very slightly alkaline 0.4*N*<sub>0</sub> sodium oleate solution which has solidified to a stiff white curd is still 95 per cent. as great as when it is a clear oily liquid at the same temperature.—M. E. L.

gelatinise, crystallise, sediment, or solidify at temperatures between  $10^{\circ}$  and  $90^{\circ}$ , as the case may be. Even potassium laurate and decoate usually separate out at above  $0^{\circ}$ . This is another reason why our chief experimental work hitherto has had to be carried out at  $90^{\circ}$ , in spite of the greatly increased difficulties entailed.

*The Conductivity of Soap Solutions at  $18^{\circ}$ .\**

In all our experiments, the precautions described in previous communications were observed. All instruments and vessels were

FIG. 1.



standardised. The soaps were likewise prepared from potassium drippings and fatty acids by methods previously described. Concentrations are expressed in weight normality,  $N_w$  (mols. per 1000 grams of water), and in volume normality,  $N_v$ , the latter referring only to the temperature of the particular experiment.

The conductivity measurements of solutions from  $N/10$  upwards were carried out in a simple and convenient cell of Jena glass of the form shown in Fig. 1, specially designed for excellent conductors. The large platinum electrodes were coated with grey

\* Experiments by M. E. L.

platinum sponge, and they were held firmly in position by glass rods fused to the cell wall and to each corner of the platinum. The cell constant was 13.20. The conductivity water possessed a specific conductivity of  $1-2 \times 10^{-6}$ , for which no correction was made. Solutions from  $N/10$  downwards were studied in the borosilicate cell described by one of us (M.E.L., T., 1918, 113, 245). The two cells gave identical values for the  $N/10$ -solutions.

The results are recorded in tables I—IV. The first column gives the weight normality,  $N_w$ , of the soap; the second, the volume normality at  $18^\circ$ ,  $N_v$ ; the third, the values obtained for the specific conductivity,  $\kappa$ , the values given being the final results from wholly independent solutions; \* the fourth,† the density,  $D_4^{18}$ ; the fifth, the equivalent conductivity,  $\Lambda$ ; the last column, the apparent degree of dissociation,  $\alpha$ , where  $\alpha = \mu_v/\mu_\infty$ ,  $\mu_\infty$  being taken as equal to 85.4 for potassium salts, except the *n*-octoate (88.2) and sodium oleate (64.3).

TABLE I.

*Conductivity of Potassium Laurate at  $18.00^\circ$ .*

$N_w$	$N_v$	$\kappa$	$\Lambda$	$\alpha$
2.000	1.378	0.05947	43.14	0.505
1.500	1.118	0.05131	45.80	0.536
1.000	0.820	{ 0.03824 } 0.03889 0.03866	47.09	0.551
0.750	0.641	0.03032	47.21	0.553
0.500	0.449	0.02042	45.44	0.532
0.400	0.367	0.01622	44.22	0.518
0.200	0.191	{ 0.007984 } 0.007984	41.77	0.489
0.100	0.098	{ 0.004322 } 0.004299	44.03	0.516
0.050	0.049	0.002713	54.89	0.643
0.0247	0.024	0.001702	68.74	0.805
0.010	0.010	0.0007539	75.44	0.883

TABLE II.

*Conductivity of Potassium Oleate at  $18.00^\circ$ .*

$N_w$	$N_v$	$\kappa$	$D_4^{18}$	$\Lambda$	$\alpha$
0.600	0.540	{ 0.02023 } 0.02013	1.0070	37.25	0.436
0.400	0.363	0.01304	1.0030	36.72	0.430
0.200	0.188	0.006243	0.9999	33.30	0.390
0.100	0.097	0.002877	0.9996	29.74	0.348
0.050	0.049	0.001451	0.9991	29.57	0.346
$N/32$	0.031	0.001035	0.9989	33.32	0.390
0.010	0.008	0.0004198	0.9987	51.95	0.608

\* One preparation of oleic acid gave quite colourless clear soap solutions, the other pale yellow solutions.

† Omitted in Tables I and IV, as new determinations were not required.

TABLE III.

*Conductivity of Sodium Oleate at 18.00°.*

$N_{20}$	$N_g$	$\kappa$	$D_4^{25}$	$\Lambda$	$\alpha$
0.600	0.510	0.01104	1.0050	21.67	0.337
0.400	0.357	{ 0.007362 0.007476 }	1.0020	20.80	0.323
0.200	0.197	{ 0.003994 0.003855 }	0.9997	19.77	0.307
0.100	0.099	0.001922	0.9993	20.46	0.318
0.050	0.049	0.0009966	0.9987	20.59	0.320
0.010	0.010	0.0002956	0.9986	30.09	0.468

TABLE IV.

*Conductivity of Potassium n-Octoate at 18.00°.*

$N_{20}$	$N_g$	$\kappa$	$\Lambda$	$\alpha$
2.000	1.601	0.06757	42.24	0.479
1.000	0.895	0.04208	48.60	0.551
0.750	0.690	0.03345	49.75	0.564
0.500	0.472	0.02455	53.00	0.601
0.200	0.198	0.01185	63.05	0.715
0.100	0.099	0.006456	69.50	0.788

The density in every case is very slightly greater than that of water, as is always observed for potassium and sodium salts of the lower fatty acids.

Some of these solutions have been measured at neighbouring temperatures by other investigators with fewer experimental precautions (Kahlenberg and Schreiner, *Zeitsch. physikal. Chem.*, 1898, 27, 552; Dennhardt, *Diss.*, 1898; *Ann. Phys. Chem.*, 1899, [iii], 67, 325; Kurtzmann, *Diss.*, 1914; *Koll. Chem. Beihefte*, 1914, 5, 465; Reyckler, Eighth International Congress of Applied Chemistry). Their results differ more or less irregularly from ours by amounts varying from 0 to 30 per cent. in both directions. The smaller differences are chiefly attributable to alkali dissolved from the glass, an important source of error in the study of soap solutions (see McBain and Taylor, *loc. cit.*, on whose exact study the validity of these experiments is based). On the whole, the agreement is substantial, and our results are probably accurate to about 1 per cent., with the possible exception of sodium oleate.

The effect of time is of the order of magnitude of 1 per cent., but all our solutions were kept for several days at the ordinary temperature to allow them to become quite constant before being measured. The data refer to clear solutions in every case, except  $N/20$ -potassium laurate, which is always cloudy. Thus many of these solutions are supersaturated or metastable with respect to



the separation of indefinite acid soaps. The latter dissolve on warming, and the metastable solutions can then be preserved for long periods.

*The Explanation of the Good Conductivity of these Colloidal Electrolytes, together with their Anomalous Maxima and Minima, by Means of the Hypothesis of the Ionic Micelle.*

It will be recollected that hydrolysis has been shown to occur to only a slight extent in concentrated solutions of soap, so that in any case it cannot be adduced to explain an appreciable part of the good conductivity exhibited by soaps (and by hexadecanesulphonic acid and its salts). This must find another explanation.

The conductivity results are best discussed by showing them in the form of a graph for comparison. This is done in Fig. 2, where the equivalent conductivities are plotted as ordinates against the concentration,  $N_v$ , as abscissæ. The figure also includes curves for the results of the higher potassium soaps at 90°.

The most striking point about these curves is that they represent moderately good conductivities even in concentrated solutions. Indeed, in many cases the conductivity curve, after passing through a minimum, rises on further concentration to a maximum, a phenomenon otherwise unknown in any aqueous solution,\* except for Reychler's hexadecanesulphonic acid, which is also a soap (*Bull. Soc. chim. Belg.*, 1913, 27, 113). This effect is more pronounced at 18° than at 90°. Again, for any one saturated fatty acid, the potassium salt exhibits this behaviour to a distinctly greater degree than does the corresponding sodium soap. The oleates differ entirely from the soaps of the saturated fatty acids in that sodium oleate is a very much more typical soap in this respect.

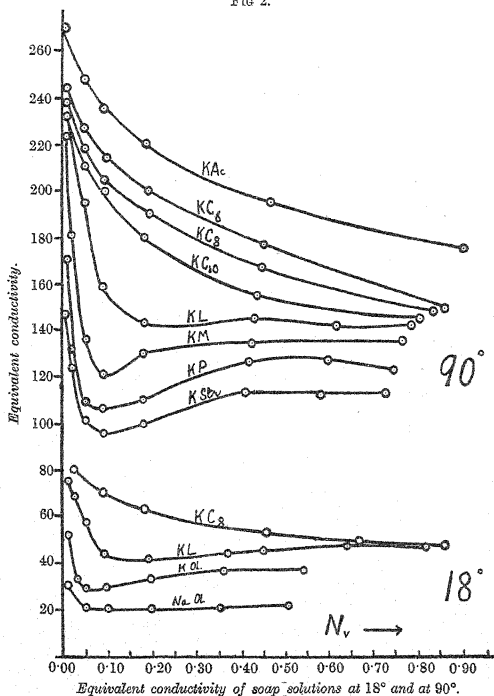
The existence of the minimum as an experimental fact has shown that on further increase of concentration the changes effected are such as to increase the conductivity. This cannot possibly be due to dissociation suddenly increasing again for a limited interval, nor can it be due to free hydroxyl ions, since the latter factor is negligibly small.

The increase of conductivity with increase of concentration must therefore be due to the replacement of the simple laurate anion by an ionic micelle of higher mobility. Thus the effect of decreasing dissociation is more than counterbalanced by this replacement. Finally, however, a maximum is reached where the steadily

\* Sloan (*J. Amer. Chem. Soc.*, 1910, 32, 946) finds that at 0° the equivalent conductivity of aqueous potassium iodide is constant over a considerable range of concentration.

diminishing dissociation of the colloidal electrolyte itself over-balances all other factors. That the conductivity of the ionic micelle is greatest in concentrated solutions, where its hydration is least, will be discussed below.

FIG. 2.



The position of the minimum at the ordinary temperature is still only at  $N/5$ , but the greater formation of ionic micelle is evinced by the quite slow rise of the curve on dilution at the solution  $N/10$  as contrasted with its rapid rise at 90°. This behaviour was predicted by McBain and Salmon, as was also the fact that

the minimum for potassium oleate occurs between  $N/10$  and  $N/20$  owing to the greater tendency of this higher soap to form micelle.

*The Temperature-coefficient of Conductivity of Solutions.*

The behaviour just described is in accordance with the abnormally high temperature-coefficient of conductivity in soap solutions, a property which was formerly ascribed to rapid increase of hydrolysis on heating, but is now seen to be the result of diminishing hydration of the ionic micelle with rise of temperature.

The influence of concentration on the temperature-coefficient of the conductivity may be analysed by the use of table V, which gives the ratios between the values at  $90^\circ$  and at  $18^\circ$ , together with those of a few electrolytes for comparison. Kurzmann (*loc. cit.*) has already pointed out that for a  $0.6N$ -potassium oleate solution the conductivity rises three-fold between  $20^\circ$  and  $90^\circ$ , whilst the viscosity falls four hundred-fold.

TABLE V.

*Ratios between Conductivities at  $90^\circ$  and  $18^\circ$ .*

Salt.	$0.01N_{90}$	$0.05N_{90}$	$0.1N_{90}$	$0.2N_{90}$	$0.5-0.6N_{90}$	$1.0N_{90}$	$2.0N_{90}$
Sodium acetate ...	3.25	3.22	3.19	3.13	3.12	3.14	3.33
Potassium acetate	2.88	2.85	2.82	2.79	2.75	2.79	2.98
Sodium hydroxide	2.53	2.46	2.46	2.44	2.45	2.50	—
Potassium							
hydroxide	—	—	—	—	—	2.22	—
Potassium octoate .	—	—	2.95	3.03	3.18	3.06	—
"    laurate	3.09	3.56	3.62	3.45	3.22	3.04	2.86

It is evident from table V that for electrolytes the ratio between the conductivities at  $90^\circ$  and  $20^\circ$  do not vary much with change of concentration, although they make a flat curve with a minimum at about half normal. Further, the values for sodium salts are in every case 0.3 unit, or about 10 per cent. higher than for the potassium salts. Soaps, on the other hand, possess higher values than the corresponding potassium electrolytes, and they exhibit an opposite behaviour in that the ratio for the temperature effect is a maximum in medium concentration. Kurzmann's ratios, as far as they go, appear to parallel ours, but are 0.3 to 0.4 unit lower.

The customary temperature-coefficients of conductivity involve three separate factors for any electrolyte and five for a colloidal electrolyte. The first two are the specific mobilities of the two ions, of which those with lowest mobility have the highest temperature-coefficient, the third is the change of dissociation with temperature, whilst in the case of a colloidal electrolyte there is

the further factor of the change in equilibrium between ions and ionic micelle in addition to the temperature-coefficient of the latter itself. The more exact analysis is simple for electrolytes, but must remain in abeyance for the soaps until we have obtained the further experimental data contemplated. The higher temperature-coefficient for sodium ion is in accordance with the recognised probability of its hydration being greater than that of potassium, and that the same factor of hydration would explain the data for soap solutions. The increase of colloid with lowering of temperature is also a factor which might conceivably operate in either direction according as to whether this is increase of highly mobile ionic micelle or increase of neutral colloid at the expense of electrolyte and micelle.

The other case of a colloidal electrolyte exhibiting an anomalous conductivity curve is hexadecylsulphonic acid (Reychler, *loc. cit.*), which exhibits a minimum conductivity of 135 mhos. (to 149 mhos.) in  $N/30$ -solution at  $56^{\circ}$  (or  $55^{\circ}$ ), but it has been measured only up to  $N/15$ -solution. Indeed, it is tantalising in the extreme to note how many promising cases of colloidal electrolytes have been studied only in dilute solution, probably the reason why this type of behaviour has not been long familiar.

#### *The Osmotic and Freezing-point Methods.*

These data are not nearly so accessible as one might expect for the case of colloidal electrolytes in which we are interested, as a brief examination will show. Indeed, the data of McBain and Salmon constitute the only satisfactory determinations hitherto recorded.

The freezing-point method, which is the subject of our present study, is the osmotic method *par excellence* where it can be applied, but it is here surprisingly limited in its range of application. Its trustworthiness is undisputed, and, further, it may be made accurate. The boiling-point method is wholly untrustworthy in its application to solutions that froth and contain colloids on account of the effects of enclosed air, which, as McBain and Taylor proved experimentally, entirely vitiate the indications of the method, and may lead to large apparent lowering instead of rise of boiling point. The vapour-pressure method, even in the hands of Smits, led to equally erroneous results on account of the same unsuspected error. McBain and Taylor found that weeks of effort were required to obtain a single rather inexact measurement. Osmometer data, again, depend so much on the mode of interpretation that it is inadvisable to build upon such a foundation.

The lowering of dew-point method has been developed by McBain and Salmon, and measurements have been made of nearly a hundred soap solutions. It possessed the double advantage that it could be used at various temperatures, and that the presence of air had no influence on the results. It is, however, an unfamiliar method which has not been previously applied to the study of solutions.

The existing literature consists of two measurements by Kahlenberg and Schreiner of the lowering of freezing point of  $N/8$ - and  $N/16$ -sodium oleate, and the dew-point data of McBain and Salmon, mostly referring to a temperature of  $90^{\circ}$ . The freezing-point measurements here presented were carried out in order to study the effect of temperature and obtain further corroborative evidence by this independent method.

The great difficulty is to measure the soaps while in the form of homogeneous solution. On cooling in the freezing apparatus, they usually become turbid, with the formation of fine, white or colourless, crystalline flakes, presumably of somewhat acid soap. This may often be avoided, and the soaps can be measured in the metastable condition. It should be noted that they are only a few degrees below the temperature at which the homogeneous form of the system constitutes stable reversible equilibrium. Indeed, perhaps the most important fact for the whole study of soap solutions is that the solutions constitute perfect reversible equilibria in which colloid, micelle, and crystalloid alike participate (see McBain and Taylor, *loc. cit.*). Incidentally, this would lead us to infer that colloidal systems in general represent the equilibria much more often than is usually recognised, owing to the conditions not being kept constant.

Two methods were used, namely, the ordinary one of Beckmann and that of Richards (*Zeitsch. physikal. Chem.*, 1903, **44**, 563; *J. Amer. Chem. Soc.*, 1903, **25**, 291). The latter is the quickest, and probably also the most accurate, of the precision methods, and it had been shown to be capable of yielding results accurate to about  $0.0003^{\circ}$ . It consists of the use of a Dewar vacuum vessel surrounded by a bath of the freezing temperature, and containing a solution which is full of finely powdered pure ice. When, after stirring, equilibria is attained, a portion of the solution is withdrawn for analysis. For the latter we used either a Zeiss interferometer in conjunction with a graph prepared from standard solutions, or else we evaporated the solutions to dryness and weighed the residue. The former method, for example, is suitable for potassium acetate, the latter for potassium laurate. Although our object was not great accuracy, but chiefly trustworthiness and

results free from distortion, we used a standard thermometer graduated in five-hundredths of a degree, the scale and readings of which were corrected to the readings on the international hydrogen thermometer at the Reichsanstalt in 1913, and this thermometer was kept permanently at  $0^{\circ}$ .

Results by the ordinary Beckmann method are usually much distorted by the effect of the low convergence temperature, which makes the lowering too great. In concentrated solutions, moreover, the alteration of concentration due to undercooling is very appreciable, and tends in the same direction. This error cannot readily be allowed for by the ordinary method of calculation in the case of soap solutions, although it is very marked, probably on account of the protective action of the colloid on incipient ice crystals. Thus, unless an inoculating rod was used, the undercooling easily exceeded  $7^{\circ}$  for an hour at a time, in spite of vigorous stirring. Great care was taken to minimise undercooling and to raise the convergence temperature. The important point to remember in what followed is that the lowering observed is never less than the true value, but that, on the contrary, the osmotic effect is exaggerated.

*The Freezing-point Data.*

Table VI presents the results of the Beckmann freezing method. The results marked with an asterisk denote turbid solutions. The potassium myristate ( $C_{14}$ ) separated out completely on cooling with marked evolution of heat; the liquid froze a few thousandths of a degree below  $0^{\circ}$ .

TABLE VI.\*

*Lowering of Freezing Point by Beckmann Method.*

	0.2N <sub>w</sub> .	0.5N <sub>w</sub> .	1.0N <sub>w</sub> .	2.0N <sub>w</sub> .
Potassium acetate.....	0.749°	1.948°	3.82°	8.56°
Sodium acetate .....	0.704	1.774	3.739	8.10
Potassium <i>n</i> -octoate...	0.742	1.860	2.519	3.146
„ decoate...	0.649	0.752	1.014	—
„ laurate ...	{ 0.197	{ 0.332	{ 0.623	{ 0.355
	{ 0.245	{ 0.371	{ 0.737	{ 1.460

Also 0.75 sodium acetate,  $2.740^{\circ}$ ; 1.5 sodium acetate,  $5.83^{\circ}$ ; 0.05 potassium laurate,  $0.177^{\circ}$ ; 0.1 potassium laurate,  $0.212^{\circ}$ ; 1.0 sodium *n*-octoate,  $2.445^{\circ}$ ; 0.6 potassium oleate,  $0.348^{\circ}$ ; 0.4 potassium oleate,  $0.215^{\circ}$ ; 0.4 sodium oleate,  $0.146^{\circ}$ ; 0.2 sodium oleate,  $0.095^{\circ}$ ; 3.0 potassium *n*-octoate,  $4.71^{\circ}$ .

\* Experiments by M. E. L. or J. W. M.

Table VII contains the results of the Richards method, in which it is a matter of great difficulty to avoid separation of soap with resulting turbidity. Here again such solutions are designated by an asterisk. Many unsuccessful attempts were made to measure clear laurate solutions until, finally, in one case a solution which had been carefully frozen without becoming turbid was introduced in this form and stirred very slowly until the temperature was constant; the liquid then withdrawn was clear.

TABLE VII.\*

*Lowering of Freezing Point (corr.) by Richards' Method.*

Potassium acetate.		Potassium acetate.		Potassium oleate.		Potassium laurate.	
0.824N <sub>w</sub>	2.934°	0.323N <sub>w</sub>	1.120°	1.196N <sub>w</sub>	0.117°	0.684N <sub>w</sub>	0.381°
0.718	2.522	0.316	1.102	0.095	0.088	0.569	0.337
0.538	1.890	0.292	1.007	0.065	0.064	0.491	0.304
0.529	1.830	0.258	0.882	Potassium n-octoate		0.175	0.182
0.488	1.712	0.234	0.800			0.124	0.168
0.469	1.635	0.206	0.690			0.0829	0.154
0.425	1.490	0.169	0.588	0.811N <sub>w</sub>	2.367	0.0361	0.120
0.378	1.324	0.146	0.507	0.509	1.912	0.456	0.328
0.352	1.230	0.113	0.404	0.405	1.534	0.262	0.242
—	—	—	—	0.269	1.004	0.121	0.203
—	—	—	—	0.169	0.610	0.093	0.164

The values obtained by the Beckmann method are in many cases higher than the more accurate data of table VII. Further, the data for solutions which have become turbid through separation of solid are distinctly less than those for clear solutions.

The lowering of freezing point indicates the total concentration of crystalloid. This is shown in table VIII for round concentrations, in most cases making use of the data of table VII in preference to those of table VI, and, of course, taking only the data for clear solutions. The numbers are obtained by dividing the lowerings by 1.858, the cryoscopic constant for water.

TABLE VIII.

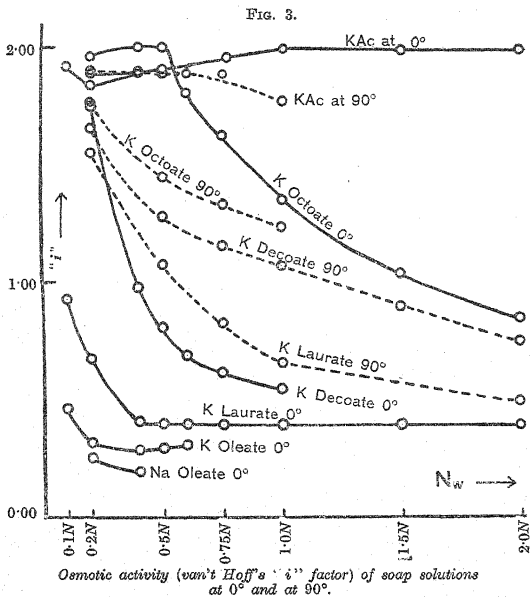
*Total Concentration of Crystalloid in these Solutions.*

	0.1N <sub>w</sub>	0.2N <sub>w</sub>	0.4N <sub>w</sub>	0.5N <sub>w</sub>	0.6N <sub>w</sub>	1.0N <sub>w</sub>	2.0N <sub>w</sub>
Potassium acetate.....	0.19	0.37	0.76	0.94	1.13	2.03	4.60
Sodium acetate .....	—	0.38	0.76	0.95	1.16	2.01	4.36
Potassium octoate ...	—	0.37	0.81	1.00	1.13	1.36	1.693
„ deoate ...	—	0.35	0.39	0.40	0.41	0.55	—
„ laurate ...	0.093	0.136	0.164	0.20	0.24	0.40	0.79
„ oleate .....	0.046	0.064	0.116	0.15	0.19	—	—
Sodium oleate .....	—	0.051	0.079	—	—	—	—

\* Experiments by A. F. T.

Also sodium octoate,  $1.0N_w$ , 1.32; potassium octoate,  $3.0N_w$ , 2.53.

The lowering of freezing point is so large as to be indisputable, although it is in many of the solutions less than for an electrolyte of the same concentration.



#### *The Effect of Temperature on the Osmotic Activity of Soaps.*

The significance of these results is more apparent from a study of the results plotted graphically, as in Fig. 3, in the form of the value of the van't Hoff factor " $i$ ." This is merely the ratio between the actual lowering and that predicted theoretically for a perfect non-electrolyte of the same concentration, namely,  $1.858^\circ$  per equivalent of normality. In Fig. 3 the values of " $i$ " are plotted against total weight normality of the solution. Some of the values at  $90^\circ$  are included for comparison.



First, with regard to the absolute magnitude of the osmotic effect in concentration of the higher soaps above  $N/3$ , it lies between  $1/5$  and  $2/5$  of that for a crystalloid such as sucrose, or between  $1/10$  and  $2/10$  of that for an acetate. Further, the osmotic effect tends to be constant for concentrated solutions. At  $90^\circ$ , on the other hand, the osmotic effect is several times greater, and it decreases rapidly with concentration up to  $1.5N$  or beyond. Both facts indicate a much more complete formation of colloid at the lower temperature.

Secondly, the familiar general influence of hydration in magnifying osmotic effects is clearly apparent in the data for the acetates, which in turn stimulate complete dissociation in concentrated solution. The effect of hydration is much more in evidence at  $0^\circ$  than at  $90^\circ$ .

The octoate is particularly interesting in its intermediate position in the homologous series as in its behaviour. In solutions up to  $N/2$ , it is quite like the acetate, although with even greater apparent hydration. From  $N/2$  upwards, however, it rapidly and steadily falls, like the decoate at  $90^\circ$ , until the osmotic activity is only  $0.85$  that of a theoretical (non-hydrated) non-electrolyte.

*The Concentration of Potassium or Sodium, and the Mobility of the Ionic Micelle at  $18^\circ$ .*

In tables I to IV, values were given for the degree of dissociation deduced from conductivity based on the mobilities  $K' = 64.7$ ,  $Na' = 43.6$ ,  $C_2' = 34.7$ ,  $C_8' = 23.5$ ,  $C_{12}' = 20.7$ ,  $C_{18}' = 20.7$ , where the fatty acid ions are indicated by the number of carbon atoms they contain. Our data, supplemented by those of Kohlrausch for the acetates, when calculated lead to the provisional concentration of alkali ions given in table IXa. This tacitly assumes that even the ionic micelle exhibits the same conductivity as the ions from which it originates. An alternative basis of calculation is contained in table IXb, to be explained below.

TABLE IX.

*Concentration of Potassium or Sodium at  $18^\circ$ .*

(a) Assuming Ordinary Ionic Mobilities.

Substance.	0.1N.	0.2N.	0.4N.	0.5N.	0.6N.	1.0N.	2.0N.
Potassium acetate.....	0.084	0.159	0.298	0.360	0.422	0.634	1.002
Sodium acetate .....	0.069	0.129	0.235	0.278	0.324	0.467	0.680
Potassium octoate ...	0.079	0.143	0.251	0.300	0.350	0.551	0.958
„ laurate ...	0.052	0.098	0.207	0.265	0.324	0.551	1.01
„ oleate .....	0.035	0.078	0.172	0.217	0.262	—	—
Sodium oleate .....	0.032	0.061	0.129	0.165	0.192	—	—

TABLE IX. (*continued*).(b) *If Ionic Micelle has the same Mobility as Potassium.*

Substance.	0.1N.	0.2N.	0.4N.	0.5N.	0.6N.	1.0N	2.0N.
Potassium octoate ...	0.079	0.143	0.251	0.300	0.342	0.504	0.822
„ laurate ...	0.034	0.065	0.137	0.176	0.214	0.36	0.66
„ oleate .....	0.023	0.051	0.114	0.143	0.173	—	—
Sodium oleate .....	0.019	0.037	0.077	0.098	0.120	—	—

Taking, first, the tentative results of table IXa for the oleates and laurate, and comparing them with the data of table VIII, it is at once apparent that the supposed concentration of potassium or sodium greatly exceeds the total concentration of crystalloidal matter present, except for the most dilute solutions. Thus, for 0.4N-solutions, the discrepancies amount to about 0.05N.

We are forced to revise the assumption made with regard to the conductivity of the ionic micelle, and to ascribe to it a conductivity equal to that of the potassium if conductivity and osmotic measurements are to be harmonised at all. In table IXb, then, the conductivity data are calculated on the assumption that the ionic micelle has an equivalent conductivity of 64.7, which is more than three times as great as that of the true oleate or oleate ion. This is, however, in agreement with the theoretical considerations advanced by one of us (J.W.M., *Trans. Faraday Soc.*, 1913, **9**, 99; *Kolloid Zeitsch.*, 1913, **13**, 56), and already applied by one of us in a previous communication with Salmon (*loc. cit.*). It was found necessary to make a similar assumption in the case of concentrated solutions at 90°.

Once again it is necessary to recall that the known sources of distortion of the experimental data operate in such direction as to emphasise the argument on which our conclusions are based. Thus, owing presumably to hydration, osmotic data in general are obviously magnified (see, for example, Landolt-Börnstein "Tabellen," where apparent dissociation frequently exceeds 100 per cent.). Again, high viscosity is conceded to have the effect of diminishing apparent conductivity. Yet, in spite of this, the outstanding experimental result is that in soap solutions the osmotic effect is only sufficient to explain about half of the conductivity exhibited.

The effects just discussed for the case of ordinary electrolytes are exemplified in the usual unmistakable fashion by the results for the acetates and the more dilute solutions of the octoate. In these cases, the osmotic activity as measured considerably exceeds the total predicted from conductivity. In the more concentrated solutions of octoate, however, the soap character predominates

sufficiently to mask this, and they show more than 50 per cent. of colloid (see below, table X).

In this intermediate case of potassium octoate in table IX $\bar{b}$  use was made of Fig. 3 in computing the average mobilities of the varying mixtures of ions and ionic micelle here present. For solutions between 0.5 and 2.0*N*, it was simply assumed that  $\Lambda_{\infty}$  varied linearly with the  $i$  value from 88.2 for  $i=2.00$  to 108.3 for  $i=0.40$ . This is a first approximation pending the results of actual measurements of migration now being carried out with soap solutions.

*The Amounts of Crystalloid and Colloid in Soap Solutions.*

The total amounts of crystalloidal matter other than potassium or sodium are obtained by subtracting the numbers in table IX $\bar{b}$  for sodium or potassium from those of table VIII for total crystalloids; the results are given in table X. Further, these amounts subtracted from the total concentration leave the amounts which it is necessary to regard as colloid. Further, since the total amount of, say, oleate present must be the sum of crystalloidal and colloidal oleate, the amount of colloid is simply the total concentration less the value for crystalloid given in table X. These values are collected in table XI, and the latter includes for comparison a few results found by the dew-point method at 90°.

TABLE X.

*Crystalloidal Matter other than Potassium or Sodium.*

Substance.	0.1 <i>N</i> .	0.2 <i>N</i> .	0.4 <i>N</i> .	0.5 <i>N</i> .	0.6 <i>N</i> .	1.0 <i>N</i> .	2.0 <i>N</i> .
Potassium acetate.....	0.106	0.211	0.462	0.580	0.708	1.396	3.598
Sodium acetate .....	—	0.251	0.525	0.672	0.836	1.543	3.680
Potassium octoate .....	—	0.248	0.559	0.700	0.790	0.856	0.868
„ laurate ...	0.059	0.071	0.027	0.02	0.03	0.04	0.13
„ oleate .....	0.023	0.013	0.002	0.007	0.014	—	—
Sodium oleate .....	—	0.014	0.002	—	—	—	—

TABLE XI.

*Total Concentration of Colloid.*

Substance.	0.1 <i>N</i> .	0.2 <i>N</i> .	0.4 <i>N</i> .	0.5 <i>N</i> .	0.6 <i>N</i> .	1.0 <i>N</i> .	2.0 <i>N</i> .
Potassium octoate	—	-0.05	-0.06	-0.2	-0.19	+0.144	+1.132
Do. at 90° .....	—	-0.02	—	+0.07	—	+0.28	—
Potassium laurate	0.041	0.129	0.373	0.48	0.57	0.96	1.87
Do. at 90° .....	—	-0.01	—	+0.22	—	+0.85	+1.89
Potassium oleate... <sup>f</sup>	0.077	0.187	0.398	0.493	0.586	—	—
Sodium oleate .....	—	0.186	0.398	—	—	—	—

The results given in tables X and XI may be summarised in the statement that in all but the most dilute solutions of the laurate, and still more so with the oleates, the soap exists almost entirely as colloid. The 0.1*N*- and 0.2*N*-laurate, and the 2.0*N*-octoate, contain comparable amounts each of crystalloid and colloid.

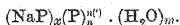
It is instructive to note that the effects of hydration are much less evident at 90°, which agrees well with the extensive investigations of H. C. Jones and others on the solvate theory. The results with soap solutions in general afford strong support for a solvate form of the dissociation theory. For instance, the change in hydration with temperature explains the very high temperature-coefficient of the conductivity of soap solution.

The second effect of temperature is that much more colloid is formed at lower temperatures. This is very evident in the case of the higher soaps. At 90°, as at the ordinary temperature, very dilute solutions of soap contain but little colloid, and the soap is essentially in the form of a simple electrolyte. At the lower temperature, however, the formation of colloid sets in at much lower concentration.

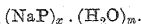
The combined influences just referred to are most apparent in the intermediate case of the octoate. Whereas at the ordinary temperature apparently negative concentrations are deduced for colloid owing to the influence of hydration, even up to 0.6*N*-solution, at 90° the negative value at 0.2*N* is almost within the experimental error, and the formation of colloid shown already at 0.5*N*-solution to the extent of 14 per cent.

#### *The Formulation and Concentration of the Ionic Micelle.*

As was shown in the previous communication, the conception of the ionic micelle that appears most probable pending the results of further experiments is that it consists essentially of an aggregation of ordinary ions retaining their original charges. Around this nucleus would be condensed a large number of molecules of water, and probably also most of the neutral colloidal soap available. This is represented in the formula



With increasing concentration, or when the dissociation is diminished, this must tend to alter towards neutral colloid



There was evidence for the conclusion that hydration diminishes and mobility increases with increasing concentration.

We have shown how the approximate values of the concentra-

tions of the total crystalloid and total colloid can be obtained. We have now to allocate the total crystalloid between undissociated soap, sodion or potassion, and simple fatty ion, and the total colloid between neutral colloid,  $(\text{NaP})_x$ , and aggregated ions in the micelle,  $(\text{P})_n^{(1)}$ .

This is at present possible only between certain limits set out in table XII below. The first figure in each pair allocates the total colloid so far as possible to micelle; this cannot, of course, exceed the concentration of potassion or sodion, and any excess must necessarily be ascribed to neutral colloid. The second figure in each case makes the opposite assumption, allotting the total colloid to neutral colloid as far as possible. The maximum here is the total amount of undissociated soap obtained by subtracting the concentration of potassion or sodion from the total concentration of the solutions; any excess of colloid must then be recognised as ionic micelle. Table XII includes previous data for the case of potassium laurate at  $90^\circ$  for comparison. Results are expressed in mols. per 1000 grams of water.

TABLE XII.

*Measured Limits of Concentration of Constituents of Soap Solutions.*

$N_{\text{st}}$	Neutral colloid, $(\text{KP})_x$	Micelle, $\text{P}_n^{(1)}$	Simple ion, $\text{P}^{\cdot}$	Simple undissociated KP.	Cation. K.
<i>Potassium Octoate at <math>0-18^\circ</math>.</i>					
1.0	0.00—0.14	0.14—0.00	0.35—0.50	0.50—0.35	0.50
2.0	0.31—1.13	0.82—0.00	0.04—0.82	0.82—0.04	0.82

*Potassium Laurate at  $0-18^\circ$ .*

0.1	0.01—0.04	0.03—0.00	0.00—0.03	0.06—0.03	0.03
0.2	0.06—0.13	0.07—0.00	0.00—0.07	0.07—0.01	0.07
0.4	0.24—0.26	0.14—0.11	0.00—0.03	0.03—0.00	0.14
0.5	0.30—0.32	0.18—0.16	0.00—0.02	0.02—0.00	0.18
0.6	0.36—0.39	0.21—0.18	0.00—0.03	0.03—0.00	0.21
1.0	0.60—0.64	0.36—0.32	0.00—0.04	0.04—0.00	0.36
2.0	1.21—1.34	0.66—0.53	0.00—0.06	0.13—0.07	0.66

*Potassium Laurate at  $90^\circ$ .*

0.2	0.00	0.00	0.10	0.10	0.10
0.5	0.00—0.22	0.22—0.00	0.04—0.26	0.24—0.02	0.26
1.0	0.33—0.48	0.52—0.37	0.00—0.15	0.15—0.00	0.52
2.0	1.00—1.11	0.89—0.78	0.00—0.11	0.11—0.00	0.89

TABLE XII. (*continued*).*Measured Limits of Concentration of Constituents of Soap Solutions.*

$N_w$	Neutral colloid, (KP) <sub>x</sub>	Micelle, $P_n^{(l)}$	Simple ion, P'	Simple undissociated KP.	Cation. K.
<i>Potassium Oleate at 0—18°.</i>					
0.1	0.05—0.08	0.02—0.00	0.00—0.02	0.02—0.00	0.02
0.2	0.14—0.15	0.05—0.04	0.00—0.01	0.01—0.00	0.05
0.4	0.28—0.29	0.11	0.00	0.00	0.11
0.5	0.35—0.36	0.14	0.00	0.00	0.14
0.6	0.41—0.43	0.17—0.16	0.00—0.01	0.01—0.00	0.17

*Sodium Oleate at 0—18°.*

0.2	0.15—0.16	0.04—0.02	0.00—0.01	0.01—0.00	0.04
0.4	0.32	0.08	0.00	0.00	0.08

An inspection of the data in table XII reveals that in the cases of the oleates and the more concentrated solutions of the laurates, the limits of concentration of each constituent are narrowly defined. These solutions consist almost entirely of colloid, together with potassium or sodium. There is more than twice as much neutral colloid, (KP)<sub>x</sub>, as of agglomerated ions,  $P_n^{(l)}$ ; in these potassium soaps and in sodium oleate there is four times as much (NaP)<sub>x</sub> as of  $P_n^{(l)}$ , whereas at 90° the proportion varied between 3/2 and nearly equal amounts.

Once more the difference between potassium and sodium soaps asserts itself, a difference that is evidence for the inclusion of the neutral colloid in the micelle, since otherwise the micelle must be of identical composition in the two cases. Although there is the same total amount of colloid in both cases, the sodium soap contains only about half as much micelle.

Comparison with solutions at higher temperatures shows that there is more neutral colloid present at low temperatures, presumably in the micelle, and possibly in the same way that there is also greater hydration at the lower temperature. This accords also with the abnormally high temperature-coefficient of conductivity.

*Comparison with Results of Dew-point Measurements at 20°.*

We have carried out a few dew-point measurements at 20° for comparison, employing the method previously described. The data

are given in table XIII. It will be noticed that the data agree exactly with the most accurate of the freezing-point data; the method is applicable at all temperatures, and therefore to all soap solutions.

TABLE XIII.

*Measurements of Lowering of Dew Point of Soap Solution.\**

Soap.	$N_w$	Temperature.	Lowering.	Crystal- loid.	" $\delta$ ."
Potassium chloride .....	1.0N	20°	0.58°	1.99	1.99
"    laurate.....	0.2	20	0.04	0.14	0.70
"    octoate .....	3.0	20	0.70	2.41	0.99
"    oleate .....	0.6	20	0.07	0.24	0.40
0.2 Potassium laurate } 0.6 "    oleate }	—	20	0.12	0.41	0.51
Ammonium laurate .....	1.0N	20°	0.17°	0.583	0.583
"    "    .....	0.5	20	0.08	0.275	0.55
"    palmitate ...	1.0	20	0.06	0.206	0.21
"    "    .....	1.0	90	0.13	0.277	0.28

The complicated effect possible when soaps are mixed in solution has been discussed elsewhere. In the case of the mixture in table XIII, 0.6N in respect of oleate and 0.2N in respect of laurate, the total concentration of crystalloid is 0.41N, as compared with 0.38N, the sum of that of the constituents separately. The conductivity of the mixture is also 5 per cent. above that of the constituents, so that most of this increase may be attributed to formation of mixed ionic micelle.

#### *Ammonium Soaps.*

The study of ammonium soap prepared from palm-kernel oil (which is largely laurate with some higher constituents) by Goldsmidt and Weismann (*Kolloid Zeitsch.*, 1913, 12, 18) has given very interesting results. Like the potassium soaps, they exhibit fairly high conductivity, which in this case cannot possibly be due to products of hydrolysis. The conductivity curve differs greatly from those of sodium and potassium soaps in that it rises steadily with concentration from 0.2N- up to 1.0N-solution by about 38 per cent. The rise is rapid at first, then more gradual. Dilute solutions were not measured. The rise is accompanied by an increase in viscosity of several hundred-fold. All these solutions are appreciably hydrolysed, as is shown by the increase in conductivity effected by addition of excess of ammonia, which in itself is a poor conductor.

These results can be interpreted as showing that the simple fatty

\* Measurements by M. E. L.

ion existing in more dilute solutions is being replaced in more concentrated solutions by the ionic micelle, which is a better conductor. This is quite in accord with our conclusions, but the micelle in concentrated solutions must conduct as well as a good conducting ion, such as potassium.

Some dew-point measurements of ammonium soaps are given in the lower half of table XIII. The solutions were prepared from pure fatty acids. It was not considered necessary to correct them for the effect of the partial pressure of the ammonia, as it was evidently too small.

In warm weather, the *N*- and *N*/2-laurates were quite clear solutions showing none of the usual appearances of soap solutions except that they gave a very good lather. On cooling, the *N*/2-laurate solution deposited feathery, crystal-like flakes; the *N*-solutions did not do this, but in very cold weather they set to a semi-transparent jelly similar to a potassium soap. The *N*/2-palmitate was somewhat similar, but the *N*-solution was practically solid at all temperatures, and resembled solid white foam.

A glance at the results shows that, independent of the temperature, there is a very large difference between ammonium laurate and palmitate—very much greater than that observed in potassium soap solutions. The total crystalloid in ammonium laurate is nearly 50 per cent. greater than in potassium laurate, whereas in ammonium laurate it is much less than in ammonium palmitate. An appreciable fraction of the total crystalloid will be undissociated ammonia.

Further investigation would evidently be well repaid, particularly if pure fatty acids were used for making the solutions and hydrolysis were avoided, as suggested above. Enough has been presented to show that the relationships agree with our general conception of colloidal electrolytes.

#### *General Conclusions and Summary.*

The theory of colloidal electrolytes defined by one of us receives further confirmation from the measurements of conductivity, freezing point, and vapour pressure of soap solutions at the ordinary temperatures here communicated.

The general theory is based on the conception, justified on mechanical grounds, that ions may be aggregated to form the nucleus of a colloidal particle, termed the ionic micelle, whilst retaining their equivalent electrical charges. Thus the ionic micelle exhibits conductivity as well as mobility even greater than the ions contained in it.



In the case of soap solutions, such as those of potassium oleate, the ionic micelle in concentrated solutions exhibits an equivalent conductivity three times greater than the oleate ion and equal to that of the potassium. Its general formula may be taken as  $(\text{KOI})_x \cdot (\text{OI})_n^{u(n)} \cdot (\text{H}_2\text{O})_m$ , the amount of water of hydration involved being least in concentrated solutions and at higher temperatures. The change in hydration explains the abnormal temperature-coefficient of conductivity.

The formation of colloid, in the case of higher soaps, is so complete at the ordinary temperature that in all ordinary solutions the only other constituent is the potassium, sodium, or ammonium, as the case may be. In dilute solutions, the soaps become simple crystalloidal salts, and hydrolysis becomes appreciable.

No other representative of this very numerous and important group of substances has yet been completely investigated, but the data available for such instances as the silicates, tellurates, dyes, proteins, salts of alkaloids, gelatin, or casein, etc., agree with the requirements of the theory, which affords a fresh interpretation and reconciliation of the results.

In conclusion, we desire to express our thanks to the Colston Society of the University of Bristol for substantial grants towards the purchase of materials and apparatus.

CHEMICAL DEPARTMENT,  
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### OXX.—*The Degree of Hydration of the Particles which Form the Structural Basis of Soap Curd, Determined in Experiments on Sorption and Salting Out.*

By JAMES WILLIAM MCBAIN and MILLICENT TAYLOR.

IN 1911 we published experiments on the salting out of sodium palmitate by sodium hydroxide, the results of which appeared to us highly remarkable (*Zeitsch. physikal. Chem.*, 1911, 76, 199, table IX). When the sodium palmitate was salted out, the clear solution that remained as mother liquor, or lye, contained a higher concentration of sodium hydroxide than before.

The explanations advanced were either that the curd which was salted out contained some acid sodium palmitate, or that very

pronounced negative sorption had occurred; and further experiments to decide this were outlined.

It is the object of this communication to present the results of the first of a series of investigations which show that salted out sodium palmitate is hydrated, and that the curd as a whole consists of this hydrated solid together with entangled or enmeshed mother liquor.

It is impossible to elucidate this<sup>a</sup> problem merely by the direct analysis of the curd, since the curd contains a quantity of concentrated lye mechanically entangled, and yet cannot be washed.

If acid soap were present, it would nevertheless be entirely masked by the large amount of free alkali in the solution clinging to it. Methods had to be devised for distinguishing the water chemically or physically combined (sorbed) from that of the enmeshed solution, thus affording a knowledge of the composition of the curd itself.

In carrying out the present experiments the concentration of the lye before and after salting out was determined, and this was supplemented by a complete analysis of the wet curds. The calculation is based upon the assumption that the sodium hydroxide is not appreciably sorbed by the hydrated curd. As will be shown, this leads to values which are only slightly less than the true degree of hydration. Methods of preparation employed and precautions observed were those previously described.

#### *The Method of Calculation of Hydration from Analysis of Lyes.*

If a system is made up by taking 1 mol. of sodium palmitate (NaP) and 1000 grams of water and 2 mols. of sodium hydroxide (thus 2.000 weight-normal,  $N_w$ ) and the curd separates out quantitatively with, say, a composition corresponding with  $\text{NaP}, 5\text{H}_2\text{O}$ , 5 mols. of water will have been abstracted from the lye. The removal of  $5 \times 18.02 = 90.1$  grams of water from the 1000 grams originally present will have resulted in an increase of the weight-normality of the solution of sodium hydroxide from the value  $N = 2.000$  to a normality  $N'$ , where

$$N' = \frac{1000}{1000 - 90.1} N.$$

Hence, in general, if  $W$  is the weight of water abstracted,

$$W = 1000 \left( 1 - \frac{N}{N'} \right) \text{ grams.}$$

If the weight-normality of the original sodium palmitate had been

$N_s$ , the hydrate or sorbed water abstracted by  $N_s$  mols. of sodium palmitate would have been

$$\frac{W}{18.02 \times N_s} \text{ mols. of water,}$$

or

$$\frac{1000}{18.02 \times N_s} \left(1 - \frac{N}{N'}\right) \text{ mols. of water to one of NaP.}$$

The residual sodium palmitate in solution in the lye amounted to only a few ten-thousandths normal, which does not affect the results.

Actually in most of the experiments, pure palmitic acid was weighed into a large silver tube and a measured volume of a concentrated solution of sodium hydroxide was added. After sealing with pure silver the tube was placed in a thermostat at about  $90^\circ$  and shaken during periods ranging from ten days to three months. The contents were then filtered through perforated silver foil at  $90^\circ$ . In carrying out the calculation outlined above, the water formed by the chemical reaction between the palmitic acid and the sodium hydroxide was taken into account, and volume was converted into weight-normality.

#### *Hydration Results from Analysis of Lyes.*

Table I presents the data of ten experiments in which sodium palmitate was salted out by sodium hydroxide. The first column contains the number of the experiment for further reference; the second, the total amount, in mols., of palmitate in 1000 grams of water, calculated as sodium palmitate; the third, the amount of sodium hydroxide in excess; the fourth, the time allowed for interaction; the fifth, the weight-normality of the sodium hydroxide in the lye after the experiment; the sixth, the amount of sorbed water to 1 mol. of sodium palmitate. In experiment 3 (*a*) previously prepared pure sodium palmitate was added to the hydroxide; in all other cases palmitic acid was added direct.

TABLE I.

#### *Hydration of Sodium Palmitate Curds at $90^\circ$ .*

No. of expt.	Original charge.		Time shaken.	Lye, NaOH N.	Hydration: mols. H <sub>2</sub> O to 1 NaP.
	NaP. N.	NaOH. N.			
1a	0.9823	2.9470	10 days	3.119	3.1
10	0.9939	2.9816	4 weeks	3.2189	3.7
Mean hydration = 3.4 H <sub>2</sub> O.					

TABLE I. (continued).

*Hydration of Sodium Palmitate Curds at 90°.*

No. of expt.	Original charge.		Time shaken.	Lye, NaOH N'.	Hydration: mols. H <sub>2</sub> O to 1 NaP.
	NaP. N.	NaOH. N.			
1	0.9608	1.9215	4 months	2.084	4.5
3	0.9608	1.9216	3 "	2.1004	4.9
6	0.9337	1.8675	10 weeks	2.042	5.0
7	0.4949	1.7919	10 "	1.898	6.3
Mean hydration = 5.2 H <sub>2</sub> O.					
3a	0.5021	1.5065	14 days	1.611	7.2
2a	0.495	1.485	10 "	1.596	8.0
11	0.5002	1.5006	4 weeks	1.566	4.7
12	0.5145	1.589	4 "	1.686	6.2
Mean hydration = 6.5 H <sub>2</sub> O.					

The results recorded in table I show clearly that there is a definite amount of combined water in each case, and that this depends on the concentration of sodium hydroxide present in equilibrium with the curd. Thus for 3.0, 1.9, and 1.5*N*-sodium hydroxide solutions the hydration is 3.4, 5.2, and 6.5 mols. of water to 1 mol. of sodium palmitate. In other words, halving the concentration of the lye has doubled the degree of hydration.

Of course, if some sodium hydroxide also is combined in the curd, the above numbers have to be slightly increased to give the true hydration values.

The result found for curd in the presence of 1.9*N*-sodium hydroxide is confirmed by an analysis of the curd itself. One hundred grams of curd contained 57.66 grams of sodium palmitate, 1.681 grams of sodium hydroxide, and 40.66 grams of water; or, to 1 mol. of sodium palmitate, 0.2027 mol. of sodium hydroxide and 10.89 mols. of water. Since the lye was shown to be 1.898*N*-sodium hydroxide, 5.93 mols. of water are to be regarded as solvent (enmeshed lye). This leaves 5.0 mols. of water of hydration to 1 mol. of sodium palmitate, as compared with the mean result, 5.2 mols., given in table I. Again, it is of interest to note that this curd contained about equal amounts of enmeshed lye and combined water.

Two further results are given in table II. Here the solution employed for salting out contained 2*N*-sodium chloride together with *N*/2-sodium hydroxide and previously prepared sodium palmitate.

The headings of the columns are as in table I, except that a

column giving the original normality of sodium chloride has been inserted after the third.

TABLE II.

*Hydration of Sodium Palmitate at 90°.*

No. of expt.	Original NaP.	Charge NaOH	NaCl.	Time shaken.	Lye NaOH.	Hydration mols H <sub>2</sub> O.
15	1.100	0.5069	2.000	2 weeks	0.5508	4.4
16	1.000	0.5069	2.000	14 days	0.5508	4.4

Mean hydration = 4.4 H<sub>2</sub>O.

This result, 4.4H<sub>2</sub>O to 1NaP, where the lye is 2.5*N* altogether, agrees excellently with the values in table I, and would make it appear that the hydration of the curd may be governed more by the concentration of the lye than by the nature of the salt employed in salting out. If this proves to be the case it will only be necessary to ascertain the molar concentration of soap lye in order to measure the hydration of commercial soap curds, once a standard value for each type has been obtained.

Results with sodium stearate are given in table III, showing that with 1.4*N*-sodium hydroxide the mean hydration is about 4.3H<sub>2</sub>O, as compared with 6.5H<sub>2</sub>O for the palmitate.

TABLE III.

*Hydration of Sodium Stearate Curd at 90°.*

No. of expt.	Original Na stearate.	Charge NaOH.	Time shaken.	Lye NaOH.	Hydration mols. H <sub>2</sub> O.
13	0.4679	1.404	46 days	1.444	3.3
14	0.4679	1.404	48 "	1.469	5.3

Mean hydration = 4.3 H<sub>2</sub>O.

*The Effect of great Pressure on the Hydration of Soap.*

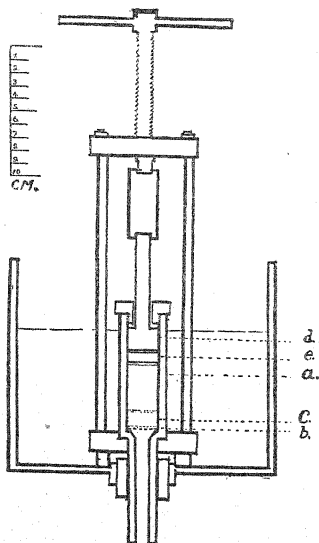
In order to leave no loophole for the alternative explanation of the phenomena here considered, experiments were carried out in which the curd was subjected to a pressure of hundreds or thousands of atmospheres during filtration. The lye filtering through was, of course, concentrated sodium hydroxide, and if the solid part of the curd really contained acid sodium palmitate, and if the separation from the curd was carried far enough, analysis of the residual curd must show a direct deficiency of alkali. However, we found that the curd was always alkaline, no matter how extreme the pressure or how much lye had been forced out. The only observed effect of applying pressure to the curd, whilst allowing the lye to escape, was to diminish the amount of hydration.

The press employed, together with the thermostat in which it was

fixed, is sketched in cross-section in the figure. The filter bed consisted essentially of sugar-carbon previously treated with lye, but arranged so as to avoid contact with the soap curd as far as possible.

The filtration was carried out in the steel tube *a*, fitted with a perforated steel filter disk, *b*.

On the top of this disk was a sheet of nickel gauze, and above



*Press employed for diminishing the hydration and imbibition of soap curd.*

that again a layer of perforated silver foil. The carbon bed, *c*, some 1—1.5 cm. in depth, rested on the foil and was covered with two more layers of the perforated silver foil. Before use the whole bed was moistened with lye and made thoroughly compact by pressure from the piston *d*.

The soap curd from which the lye had been rapidly filtered, through a silver cone, at 90°, was transferred to the filter and covered with two layers of perforated silver foil. Between this and

the steel piston was inserted a hollowed out, thick-walled rubber washer of the form used in a Bramah press. Pressure was applied through the screw by means of a double set of levers, about 80 cm. in length.

The sample of curd for analysis was taken from the centre of the block of hard curd left in the press. In satisfactory experiments it contained no carbon. Various methods were employed in the analysis, but only the one found most convenient is here described.

The curd was dissolved in neutral, boiled-out 80 per cent. alcohol containing phenolphthalein. The solution was titrated with *N*/10-sulphuric acid, the alcohol evaporated, and excess of *N*-sulphuric acid added. After decomposition of the soap had been completed by alternate heating and cooling, the solid palmitic acid was collected. The filtrate was titrated to ascertain the amount of sodium palmitate which had been present. In many cases the palmitic acid was determined directly by weighing or by titration in alcoholic solution. Water was always obtained by difference. The method of calculation was usually that illustrated by the curd analysis accompanying table I above. This is termed "mixed" calculation in the table above.

In a few cases, however, the concentration of lye after salting out was not determined. Here the amount of lye and its concentration were calculated from the analysis of the curd by successive approxi-

TABLE IV.

*Hydration of Curds after Great Pressure at 90°.*

No. of expt.	Original charge.		Curd composition : 100 grams of curd contain			Method of calculation.	Hydration : mols. H <sub>2</sub> O: to 1NaP.
	NaP. <i>N.</i>	NaOH. <i>N.</i>	NaP.	NaOH.	H <sub>2</sub> O.		
10	0.994	2.98	83.644	0.899	15.457	"Mixed"	1.547
4	0.997	1.99	77.580	1.154	21.266	"Curd"	1.42
1	0.961	1.92	(73.850	1.286	24.864)	"Mixed"	2.0
			(74.424	1.383	24.193)		1.6
2	0.961	1.92	(69.99	1.021	28.994)	"Curd"	3.6
			(67.23	1.306	31.479)		3.5
			(77.51	1.153	21.342)		(1.3 pressed on tile)
3	0.961	1.92	66.146	1.235	32.619	"Mixed"	4.3
6	0.934	1.87	(68.404	1.329	30.267)	"Mixed"	3.3
			(67.616	1.314	31.070)		3.4
			(81.913	2.084	16.003)		— 1.8 (pressed on tile)
7	0.495 Sodium stearate	1.79	73.804	0.785	25.411	"Mixed"	3.2
13	0.468	1.404	70.682	1.227	28.091	"Mixed"	1.6
14	0.468	1.404	72.916	0.905	26.179	"Mixed"	2.5

mations based on the hypothesis that all excess of hydroxide was contained in the lye and not in the curd proper. As may be shown theoretically, this leads to a perfectly defined result for the value of the hydration. This we term the pure "curd" calculation.

The results for sodium palmitate salted out by sodium hydroxide are given in table IV. The pressure was different in each case, since it depended on the condition of the filter bed, pressure being applied until the curd began to be forced through. (In one or two cases some carbon was mixed with the curd.) Several samples at different levels were taken for analysis in some of the experiments. Table V gives similar data for the pressed curds of Experiments 15 and 16 of table II.

TABLE V.

No. of expt.	Curd composition: 100 grams contain			Method of calculation.	Hydration: mols. H <sub>2</sub> O to 1 NaP.
	NaP.	NaOH.	NaCl.		
15	80.01	0.144	0.761	"Mixed"	2.2
16	80.43	0.160	0.922	"Mixed"	2.2

On examining the results of tables IV and V it appears that the very great pressure to which the curds were subjected while in contact with residual lye lowers the degree of hydration to about half of that of the unpressed curd. This is in accordance with the recognised property of colloids that the swelling pressure increases enormously as the solvent is removed, although the pressures here employed far transcend those hitherto investigated.

The most effective way of dehydrating soap curd is to press it on a porous tile, thus making use of the swelling pressure of kaolin to abstract the water. Curds from Experiments 2 and 6 so treated and the composition calculated as before, gave values for apparent hydration of 1.3 and -1.8 mols. of water respectively; this appears to show that the residual lye had also been greatly concentrated in the process owing to hydroxide being left when the water was absorbed.

### Summary.

Marked negative sorption of sodium hydroxide occurs when soap is salted out by sodium hydroxide in concentrated solution.

From the extent of this effect the amount of water contained in the solid part of the curd, as distinguished from the entangled lye clinging to it, may be deduced. Soap curd is thus shown to be a mechanical mixture of hydrate (or sorption compound) and enmeshed lye.



The degree of hydration varies with the concentration of lye as follows:

Lye.	Sorption compound.	Percentage of fatty acid.
3.0N	NaP, 3.2H <sub>2</sub> O	76.28
2.5	NaP, 4.4H <sub>2</sub> O	71.67
1.9	NaP, 5.2H <sub>2</sub> O	68.89
1.5	NaP, 6.5H <sub>2</sub> O	64.81

Extreme pressure lowers the degree of hydration considerably.

In conclusion, we have pleasure in thanking the Colston Society of the University of Bristol for a generous grant towards the purchase of materials and apparatus.

THE CHEMICAL DEPARTMENT,  
BRISTOL UNIVERSITY.

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### CXXI.—*Reaction of the Potassium Salts of 2-Thiol 5-thio-4-phenyl-4 : 5-dihydro-1 : 3 : 4-thiodiazole and 2 : 5-Dithiol-1 : 3 : 4-thiodiazole with Halogenated Organic Compounds.*

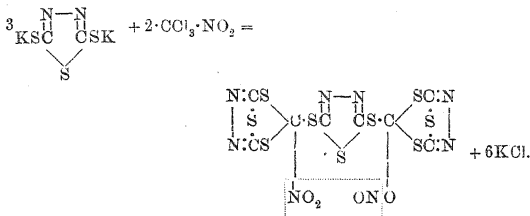
By PRAFULLA CHANDRA RÂY, PRAFULLA CHANDRA GUHA, and  
RADHA KISHEN DAS.

GABRIEL (*Ber.*, 1877, 10, 185) and Holmberg (*Ber.*, 1907, 40, 1740) treated sodium ethylmercaptide with chloroform and obtained ethyl orthotrithioformate, CH(SET)<sub>3</sub>. In the present investigation, it will be shown that the potassium atom of the complex cyclic mercaptides named in the title is singularly reactive towards the halogen atoms of organic compounds of divers types. Thus, chloroform, bromoform, and iodoform yield compounds with the potassium monomercaptide, which may be represented by the general equation  $3RK + CHX_3 = 3KX + CHR_3$ , where X represents a halogen atom and R the radicle of the complex mercaptide. Chloropicrin acts exactly like chloroform, but is far more reactive than the latter, and the reaction may be expressed by the equation  $3RK + NO_2 \cdot CCl_3 = NO_2 \cdot CR_3 + 3KCl$ .

The behaviour of tribromoresorcinol, benzylidene chloride, monochloroacetic acid, and ethylene bromide has also been found to be of an identical nature. The potassium salt of 2 : 5-dithiol-1 : 3 : 4-

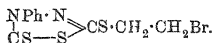
thiodiazole, on the other hand, acts almost as an inert substance towards chloro-, bromo-, and iodo-form.

It is evident that the presence of the two  $\cdot\text{SK}$  groups of the dimercaptide exercises a sort of inhibitory influence on the halogen atoms. The reactivity of these halogenated compounds can, however, be materially enhanced by substituting the remaining hydrogen atom by a nitro-group. For instance, chloropicrin acts very readily on the dimercaptide even in the cold. The introduction of an additional negative group has thus a marked effect. The reaction may be represented as follows:



Nitrous fumes escape during the reaction, and an atom of oxygen, as shown above, forms the connecting link between the two carbon atoms of the residues of two molecules of chloropicrin.

Ethylene bromide acts on the potassium monomercaptide; only one atom of bromide combines with the potassium atom, resulting in the formation of the compound,



Monochloroacetic acid, benzylidene chloride, and ethylene bromide no doubt act on the dimercaptide, but the products of the reaction are insoluble in the ordinary solvents, and thus cannot be purified.

## EXPERIMENTAL.

*Potassium Salt of 2-Thiol-5-thio-4-phenyl-4:5-dihydro-1:3:4-thiodiazole and Iodoform, Bromoform, and Chloroform.*

Three molecular proportions of the mercaptide were treated with one molecular proportion of the halogenated compound in alcoholic solution, the mixture being boiled under reflux on the water-bath for several hours. An insoluble mass was obtained consisting of the potassium haloid and the organic derivative. The solution was

allowed to cool and then triturated with water. The aqueous filtrate on evaporation gave crystals of the potassium haloid. The insoluble portion was dried and dissolved in benzene; on evaporation of the solvent, an oily liquid was obtained, which was redissolved in benzene and precipitated by alcohol as an oil. On keeping, the oil solidified to a yellow powder. As it was difficult to get rid of the last trace of iodoform, the powder was repeatedly washed with alcohol and dried in the steam-oven until the odour of iodoform was no longer perceptible. The substance melted at 66—68°.

With bromoform, exactly the same method was followed, but, as it is highly volatile, the excess was easily removed from the yellow compound, which melted at 66—68°.

When the reaction mixture in alcoholic solution was heated at 210—220° in a sealed tube for several hours, a tarry, resinous mass was obtained, which was collected and dissolved in benzene. Addition of alcohol to the benzene solution gave the same tarry precipitate, but not the yellow powder. The alcoholic mother liquor, on concentration, gave shining, needle-shaped crystals which melted sharply at 62°. Analysis proved this product to be the alcoholate of the compound described above, having the formula  $\text{CHR}_{3,2}\text{EtOH}$ . The yield was very poor, most of the product having evidently become resinified owing to the high temperature employed. No reaction took place when chloroform was heated under reflux with the mercaptide in alcoholic solution. The mixture was therefore heated in a sealed tube as in the case of bromoform. The filtrate, separated from the resinified mass, gave, on evaporation, crystals of the alcoholate melting at 62°:

0.1520 gave 0.2532  $\text{CO}_2$ .  $\text{C}=45.23$ .

0.1101 „ 11.4 c.c.  $\text{N}_2$  at 32° and 760 mm.  $\text{N}=11.26$ .

0.1260 „ 0.3532  $\text{BaSO}_4$ .  $\text{S}=38.48$ .\*

$\text{C}_{25}\text{H}_{16}\text{N}_8\text{S}_9, 2\text{EtOH}$  requires  $\text{C}=44.6$ ;  $\text{N}=10.85$ ;  $\text{S}=37.50$  per cent.

It is thus evident that iodoform and bromoform are more reactive towards the mercaptide than is chloroform.

Compound, m. p. 66—68°, from iodoform :

\* It may be necessary to point out that in these compounds the sulphur atom is linked both to an aliphatic and to an aromatic and cyclic residue. Carius's method gave an unusually low result, owing to the formation of sulphonic acid. The excess of nitric acid was therefore neutralised with sodium carbonate and evaporated to dryness and fused in a silver dish. The product was evaporated several times with hydrochloric acid before the addition of barium chloride. Owing to the presence of a large amount of sodium chloride and unchanged sodium nitrate, the result is generally a little too high.

0.0953 gave 0.1502  $\text{CO}_2$  and 0.0202  $\text{H}_2\text{O}$ .  $\text{C}=42.98$ ;  $\text{H}=2.33$ .

0.0876 „ 0.2087  $\text{BaSO}_4$ .  $\text{S}=41.19$ .

0.075 „ 8.3 c.c.  $\text{N}_2$  at  $24^\circ$  and 760 mm.  $\text{N}=12.50$ .

$\text{C}_{25}\text{H}_{18}\text{N}_6\text{S}_9$  requires  $\text{C}=43.60$ ;  $\text{H}=2.76$ ;  $\text{S}=41.80$ ;  $\text{N}=12.21$   
per cent.

The compound from bromoform gave  $\text{C}=43.11$ ;  $\text{H}=2.03$ ;  $\text{N}=12.59$  per cent.

*Potassium Salt of the Mercaptan and Chloropicrin.*

The alcoholic solution of the parent substances was heated at  $50^\circ$  under reflux as before. A bulky, yellow precipitate was obtained; after decanting off the mother liquor, it was washed with alcohol and triturated with water to remove potassium chloride. It crystallised from hot benzene in shining, yellow crystals melting at  $128-129^\circ$ . The reaction was almost quantitative, as was proved by weighing the potassium chloride formed:

0.1140 gave 0.1727  $\text{CO}_2$  and 0.0307  $\text{H}_2\text{O}$ .  $\text{C}=41.31$ ;  $\text{H}=2.99$ .

0.0948 „ 11.4 c.c.  $\text{N}_2$  at  $32^\circ$  and 760 mm.  $\text{N}=13.18$ .

$\text{C}_{25}\text{H}_{15}\text{O}_2\text{N}_7\text{S}_9$  requires  $\text{C}=40.97$ ;  $\text{H}=2.05$ ;  $\text{N}=13.37$  per cent.

*Potassium Salt of the Mercaptan and Tribromoresorcinol.*

The substances were heated in alcoholic solution as before. The amorphous powder obtained was freed from potassium bromide by water, dried, and dissolved in a mixture of alcohol and carbon disulphide; on evaporation, shining crystals melting at  $166^\circ$  were obtained:

0.0881 gave 0.1458  $\text{CO}_2$  and 0.0236  $\text{H}_2\text{O}$ .  $\text{C}=45.13$ ;  $\text{H}=2.97$ .

0.0724 „ 0.1897  $\text{BaSO}_4$ .  $\text{S}=36.00$ .

$\text{C}_{30}\text{H}_{18}\text{O}_2\text{N}_6\text{S}_9$  requires  $\text{C}=46.03$ ;  $\text{H}=2.30$ ;  $\text{S}=36.55$  per cent.

*Potassium Salt of the Mercaptan and Benzylidene Chloride.*

The components in alcoholic solution were heated under reflux for about an hour. The crystalline product melted at  $59-62^\circ$ :

0.0708 gave 0.1321  $\text{CO}_2$  and 0.0193  $\text{H}_2\text{O}$ .  $\text{C}=50.87$ ;  $\text{H}=3.03$ .

0.0849 „ 8.6 c.c.  $\text{N}_2$  at  $22^\circ$  and 760 mm.  $\text{N}=11.02$ .

0.0974 „ 0.2550  $\text{BaSO}_4$ .  $\text{S}=35.83$ .

$\text{C}_{23}\text{H}_{16}\text{N}_4\text{S}_8$  requires  $\text{C}=51.11$ ;  $\text{H}=2.96$ ;  $\text{N}=10.40$ ;  $\text{S}=35.55$   
per cent.

*Potassium Salt of the Mercaptan and Ethylene Bromide.*

After heating in alcoholic solution as usual, the insoluble product was freed from potassium bromide by means of water, dried, and dissolved in ether. On evaporation, shining crystals melting at  $94^{\circ}$  were obtained:

0.1644 gave 0.2183  $\text{CO}_2$ .  $\text{C}=36.21$ .

0.0812 „ 6.6 c.c.  $\text{N}_2$  at  $30^{\circ}$  and 760 mm.  $\text{N}=8.97$ .

0.1303 „ 0.0715  $\text{AgBr}$ .  $\text{Br}=23.35$ .

$\text{C}_{10}\text{H}_9\text{N}_2\text{BrS}_3$  requires  $\text{C}=36.03$ ;  $\text{N}=8.40$ ;  $\text{Br}=24.02$  per cent.

*Potassium Salt of the Mercaptan and Monochloroacetic Acid.*

On mixing the components in aqueous solution, the reaction takes place even in the cold, and is completed on heating. The product crystallises from boiling water in silky needles melting at  $145^{\circ}$ :

0.1279 gave 0.1935  $\text{CO}_2$  and 0.0414  $\text{H}_2\text{O}$ .  $\text{C}=41.26$ ;  $\text{H}=3.60$ .

0.1697 „ 15.00 c.c.  $\text{N}_2$  at  $24^{\circ}$  and 760 mm.  $\text{N}=9.99$ .

0.1580 „ 0.3495  $\text{BaSO}_4$ .  $\text{S}=30.38$ .

$\text{C}_{10}\text{H}_9\text{O}_2\text{N}_2\text{S}_3$  requires  $\text{C}=42.06$ ;  $\text{H}=2.81$ ;  $\text{N}=9.86$ ;  $\text{S}=33.81$  per cent.

It is of interest to note that whilst monochloroacetic acid behaves in the above manner, dichloro- and trichloro-acetic acids, on the other hand, behave like strong acids, such as hydrochloric acid, that is, they simply regenerate the original mercaptan.

*Potassium Salt of 2:5-Dithiol-1:3:4-thiadiazole and Chloropicrin.*

The components were heated under reflux in alcoholic solution for several hours. Nitrous fumes were evolved and a yellow precipitate was obtained. On cooling, this was collected and washed with alcohol to remove adhering chloropicrin, and then triturated with water to move potassium chloride. The yellow powder was insoluble in nearly a dozen ordinary solvents and in mixtures of some of them. Two different preparations had, however, the same melting point ( $166$ — $168^{\circ}$ ) and the same percentage composition:

0.1734 gave 0.1274  $\text{CO}_2$ .  $\text{C}=20.04$ .

0.0853 „ 14.00 c.c.  $\text{N}_2$  at  $31^{\circ}$  and 760 mm.  $\text{N}=18.03$ .

0.0899 „ 0.3907  $\text{BaSO}_4$ .  $\text{S}=59.68$ .

$\text{C}_8\text{ON}_6\text{S}_9$  requires  $\text{C}=19.83$ ;  $\text{N}=17.40$ ;  $\text{S}=59.50$  per cent.

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CXXII.—*Equilibria Across a Copper Ferrocyanide and an Amyl Alcohol Membrane.*

By FREDERICK GEORGE DONNAN and WILLIAM EDWARD GARNER.

DONNAN and Allmand (T., 1914, 105, 1941) investigated the distribution equilibrium of potassium and chlorine ions across a copper ferrocyanide membrane. In the method adopted, a solution of potassium ferrocyanide was placed on one side of the membrane and a solution of potassium chloride on the other. The results, whilst affording undoubted confirmation of Donnan's theory (*Zeitsch. Elektrochem.*, 1911, 17, 572), were complicated by the uncertainty as to the manner of ionisation of potassium ferrocyanide. It was considered that this difficulty would be overcome if solutions of two ferrocyanides were employed on the two sides of the membrane, especially if these salts were ionised to the same extent. In the present investigation, the sodium, potassium, and calcium salts were found to be suitable, and mixtures of these were used to test the validity of the theory.

With a mixture of sodium and potassium ferrocyanides, equilibrium will be set up by an interchange of sodium and potassium ions, since the membrane is not permeable to ferrocyanogen ions. Assuming that the ions obey the laws of ideal solutions, the equation for the equilibrium is given by

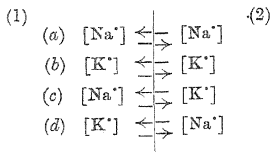
$$[\text{Na}_1'] [\text{K}_2'] = [\text{Na}_2'] [\text{K}_1'],$$

where the symbols indicate molar ionic concentrations.

This equation was derived from thermodynamical considerations by Donnan (*loc. cit.*), and its derivation is also possible from the kinetic theory, as follows: The number of ions of any one kind penetrating the membrane is proportional to its ionic concentration,  $C_1$ ; the number of ions exchanging across the membrane is proportional, not only to the concentration,  $C_1$ , but also to the concentration of the ion,  $C_2$ , which interchanges with the first across the membrane, that is,

$$N = K \cdot C_1 \cdot C_2.$$

In the case of sodium and potassium ions, at distribution equilibrium four kinds of interchanges across the membrane are possible. Two of these, (a) and (b) (exchange of like ions), do not affect the final concentrations in any way. The four interchanges are shown below:



At equilibrium, the number of exchanges due to (c), that is,  $N_c = K[\text{Na}_1^+][\text{K}_2^+]$ , must equal that due to (d), that is,  $N_d = K[\text{Na}_2^+][\text{K}_1^+]$ , therefore  $[\text{Na}_1^+][\text{K}_2^+] = [\text{Na}_2^+][\text{K}_1^+]$ .

When the calcium salt is substituted for the potassium salt, the equation of equilibrium becomes:

$$(a) [\text{Ca}_1^{++}][\text{Na}_2^+]^2 = [\text{Ca}_2^+][\text{Na}_1^+]^2,$$

and

$$(b) [\text{Ca}_1][\text{Na}_2]^2 = [\text{Ca}_2][\text{Na}_1]^2,$$

if the degree of ionisation of the two salts is the same.

In the case of the sodium-potassium cells which were investigated, the experimental results showed good agreement with the requirements of the theory.

The degrees of ionisation of the two salts are very similar, so that the ratio of the molar concentrations of the salts is the same as that of the ionic concentrations.

The sodium-calcium cells, however, gave unexpected results. Whereas the equation (b), which refers to the concentrations of the two salts, holds within the limit of the experimental error of the analysis, it was found that equation (a) above does not accurately represent the relationship between the ionic concentrations of the calcium and sodium salts on the two sides of the membrane. The activities of the ions in this case appear to be more closely related to the molar than to the ionic concentrations. This result also may indicate that adsorption plays an important part in the transference of the ions across the membrane.

Further experiments were carried out in order to find a liquid membrane which would be permeable to one electrolyte and impermeable to a second which contains an ion common to the first. With this purpose in view, the solubilities of several salts in moist, organic solvents were determined. Amyl alcohol was found to be the most satisfactory of these solvents, and potassium and lithium chlorides the most suitable electrolytes. Since lithium chloride is readily soluble in amyl alcohol (a saturated solution is 1.83*N*) and potassium chloride is practically insoluble (a saturated

solution is 0.0048*N*),\* it was hoped to set up a cell of the following type:

I. KCl, LiCl in water | Amyl alcohol | LiCl in water II.

which is of the same type as that investigated by Donnan and Allmand with the copper ferrocyanide membrane.

It was not, however, practicable to use an amyl alcohol membrane, owing to the slow rate of diffusion of lithium chloride through the amyl alcohol. The problem was therefore approached in an indirect manner. Determinations were made of the distribution concentrations of lithium chloride between amyl alcohol and water at 25°. Aqueous solutions of lithium chloride and lithium and potassium chlorides were shaken with amyl alcohol, and the two layers separated and analysed. The concentration of the lithium chloride in II, which is in equilibrium with a mixture of the two chlorides in I, was calculated from these results.

The calculation of the ionic concentrations is complicated by the high values of the viscosity of the solutions and by changes in the state of hydration of the lithium ion with concentration. Green (T., 1908, 93, 2023) has deduced the degree of ionisation of concentrated lithium chloride solutions from measurements of the conductivity of solutions of lithium chloride of which the viscosity has been increased by means of sucrose. The chief objection to the values which are obtained in this way lies in the hydration of the lithium ion, which will be affected by the addition of sucrose to the solutions.

The concentrations of the ions and the undissociated part of the electrolyte have, however, been calculated, using Green's values for the degree of ionisation of lithium chloride, and the results are in fairly satisfactory agreement with theory. The agreement is better in those cases where the total concentration of the electrolytes is below 5*N*. Thus  $[\text{LiCl}]_1 = [\text{LiCl}]_2$  and

$$[\text{Li}^+] \cdot [\text{Cl}_1'] = [\text{Li}_2'] \cdot [\text{Cl}_2'].$$

The distribution-coefficient of lithium chloride between amyl alcohol and water has been calculated, and it appears that lithium chloride occurs in amyl alcohol solution as double molecules. The coefficient is, however, only a constant over a small range of concentration, and above 5*N* the coefficient increases. The increase is probably associated with errors in the degree of ionisation due to the dehydration of the lithium ion.

The experimental work in this paper leads to the conclusion that the same equilibrium relationships are established, whether the

\* Moist amyl alcohol.



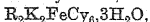
equilibrium is brought about by the transference of ions, as is the case with the copper ferrocyanide membrane, or by the transference of the undissociated part of the electrolyte, as is the case with the amyl alcohol membrane.

#### EXPERIMENTAL.

The osmometer vessels used in the determination of the ratios of the ions were those described by Donnan and Allmand (T., 1914, 105, 1944). The copper ferrocyanide membrane in parchment paper was clamped in position between two shallow, cylindrical vessels, and was separated from the supporting rim by rubber bands. The vessels, which were of Jena glass, were fitted with side-tubes to facilitate the introduction of the solutions, and the volume of each vessel was about 100 c.c. The membranes were prepared by the method described by Donnan and Allmand (*loc. cit.*), and the parchment paper was usually left in contact with the solutions for two days. The membranes were tested for leaks by placing a ferrocyanide solution on one side and an isotonic solution of sucrose on the other, and no leakage occurred over a period of six weeks.

The ferrocyanides which were used in the investigation were purified by crystallisation from water. The calcium and ammonia ferrocyanides were prepared from hydroferrocyanic acid (Noyes and Johnston, *J. Amer. Chem. Soc.*, 1909, 31, 991).

Since potassium ferrocyanide forms insoluble double salts with magnesium and calcium ferrocyanides, of the type



it was not possible to use potassium ferrocyanide against these salts in the cells. The precipitation of the insoluble salts takes place slowly at the ordinary temperature, but quicker on heating, as if a chemical change were taking place. The double salts with sodium ferrocyanide are soluble in water.

#### *Potassium-Sodium Ferrocyanide Cells.*

Solutions were used of a strength 0.025 molar. The usual procedure was to place a solution of potassium ferrocyanide in one side of the cell and a solution of sodium ferrocyanide in the other. The time required for the attainment of equilibrium was determined by conductivity measurements, and no change in the conductivity could be observed after an interval of one week. The cells were, however, allowed to remain, with occasional shaking, over a period of three to five weeks, in which time equilibrium was certain to have been reached.

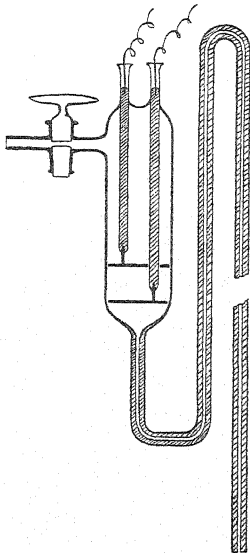
In order to prevent changes in the ferrocyanide solutions with time, several precautions were necessary.

(1) When pieces of well-washed copper ferrocyanide membrane were placed in solutions of ferrocyanides, it was observed that the strength of the solutions diminished several per cent. in three or four days, and at the same time the presence of sulphates in the solutions was detected. The change was almost entirely due to that side of the membrane which was last exposed to the copper sulphate solution. The adsorbed copper sulphate on this side of the membrane reacted with the ferrocyanide solutions, with the formation of sulphates and a slight increase in the thickness of the membrane. The copper ferrocyanide membrane, after being clamped in position, was on this account washed for three to four days with ferrocyanide solutions of the same concentrations as those to be used in the experiment.

(2) Another source of trouble was the oxidation of the ferrocyanides by the small quantity of air enclosed in the osmometer vessels. The oxidation was also considerable if the conductivity of the solutions was measured from time to time in the ordinary conductivity vessels. To make the change due to this cause as small as possible, a special conductivity vessel was constructed (Fig. 1) which could be filled with nitrogen. The amount of air in the osmometer vessel was also reduced to a fraction of a c.c., and in the majority of the experiments, of which the results are given in the tables, the cells were not opened until immediately before analysis.

(3) When solutions of different concentrations were employed on the two sides of the membrane, osmosis of water was prevented by the addition to the solution of the requisite amount of sucrose. The amounts which were added were calculated from conductivity

FIG. 1.



data. The effect due to this cause is, however, small, as Donnan and Allmand have shown (*loc. cit.*).

The solutions were kept in the dark and the cells shaken every two or three days.

#### *Method of Analysis.*

The solutions of the ferrocyanides were decomposed with concentrated sulphuric acid, and the sulphates of the alkali metals converted into chlorides by the precipitation of the iron (twice) with ammonia, and of the sulphate with a slight excess of barium chloride. After the removal of the barium as carbonate, the mixed chlorides in the solution were obtained by evaporation and weighed. The potassium was determined as perchlorate and the sodium calculated by difference.

The ferrocyanide concentrations were determined before filling into the cells, and after the equilibrium had been reached, by titration against potassium permanganate solution. These analyses serve as a check on the results obtained by the gravimetric analysis. The variation in the ferrocyanide concentrations as determined by the three methods outlined above rarely exceeded 1 per cent.

A method of analysis based on a conductivity method was not found to give the requisite degree of accuracy.

The results for the potassium-sodium cells are given in table I. The weights of potassium chlorate and the mixed chlorides are given (in order to indicate the possible errors of the analyses), and in columns 6 and 7 are included the molar concentrations of the sodium and potassium on both sides of the membrane *A* and *B*. In column 8 is found the total concentration of the metals, and in 9 and 10 four times the total concentration of ferrocyanogen before and after the experiment. The results show that no large amount of oxidation or absorption of the salts has taken place during the period of the experiment. The ratios of the sodium and the potassium in the solutions on the two sides of the cell are compared in the last column, and it will be observed that the ratio is the same for (*a*) and (*b*) within experimental error. The ratio of the ionic concentrations will be but little different from those given in the table, since the degrees of ionisation of the sodium and potassium ferrocyanides are very similar. The conductivity of 0.025 molar solutions of potassium, sodium, and ammonium ferrocyanides was determined at 25°, and the degree of ionisation calculated. The results are given in table II.

TABLE I.  
*Potassium and Sodium Ferrocyanide Cells.*

Cell No.	Weights of				Normality of				$\frac{[\text{Na}]}{[\text{K}]}$	
	KClO <sub>4</sub>	NaCl. K	NaCl.	KCl.	Na.	K.	Na + K.	$\frac{4\text{Fe}(\text{CN})_6}{\text{before.}}$		$\frac{4\text{Fe}(\text{CN})_6}{\text{after.}}$
1 a.....	0.3123	0.2659	0.0979	0.1680	0.0335	0.0451	0.0786	0.0794	0.0793	0.743
b.....	0.3145	0.2656	0.0965	0.1691	0.0410	0.0567	0.0977	0.0995	0.0995	0.723
2 a.....	0.2064	0.1992	0.0881	0.1111	0.0503	0.0497	0.1000	0.0990	0.0982	1.012
b.....	0.2069	0.1982	0.0869	0.1113	0.0496	0.0498	0.0994	0.1000	0.0979	0.996
3 a.....	0.1984	0.1973	0.0905	0.1068	0.0516	0.0477	0.0993	0.1000	0.0998	1.082
b.....	0.2181	0.2181	0.1007	0.1174	0.0575	0.0524	0.1099	0.1105	0.1095	1.097
4 a.....	0.1839	0.1970	0.0980	0.0990	0.0559	0.0443	0.1002	0.1001	0.1001	1.262
b.....	0.2163	0.2332	0.1168	0.1164	0.0666	0.05205	0.1187	0.1199	0.1192	1.280
5 a.....	0.1731	0.1935	0.1004	0.0931	0.0573	0.0416	0.0989	0.1005	0.0992	1.377
b.....	0.1785	0.1993	0.1033	0.0960	0.0884	0.0643	0.1527	0.1506	0.1498	1.375

TABLE II.

*Degree of Ionisation of Ferrocyanides.*

Salt.	$\Lambda_{\infty=40}$ .	$\Lambda_0$ Kohl- rausch.	100 $\alpha$ .
$(\text{NH}_4)_4\text{Fe}(\text{CN})_6$ .....	333.1	742.0	51.6
$(\text{Na})_4\text{Fe}(\text{CN})_6$ .....	337.1	647.6	52.1
$(\text{K})_4\text{Fe}(\text{CN})_6$ .....	393.0*	742.0	52.9

\* Noyes.

Thus the relationship given below has been proved to be correct, that is,

$$\frac{[\text{Na}_1^*]}{[\text{Na}_2^*]} = \frac{[\text{K}_1^*]}{[\text{K}_2^*]}.$$

Since the activities of the potassium and sodium ions are probably very similar, the equation deduced by Donnan has been shown to hold.

*Sodium-Ammonium Cells.*

Ammonium ferrocyanide solutions slowly attack the copper ferrocyanide membrane. The membrane thickens and changes in colour from a dark brown to a reddish-brown. It does not, however, appear to break down, as on one occasion a cell was made up of a solution of ammonium ferrocyanide on the one side and an isotonic sucrose solution on the other. After five weeks, the sucrose solution was tested, and it was found that no ferrocyanide had diffused through the membrane. The concentration of ferrocyanide had, however, diminished, and the colour of the membrane on the one side had changed to a reddish-brown. In consequence of these irregularities, only one sodium-ammonium cell was examined. The ratio  $\frac{[\text{Na}]}{[\text{NH}_4]}$  on the two sides were found to be 0.8480 and 0.8595 respectively.

*Sodium-Calcium Cells.*

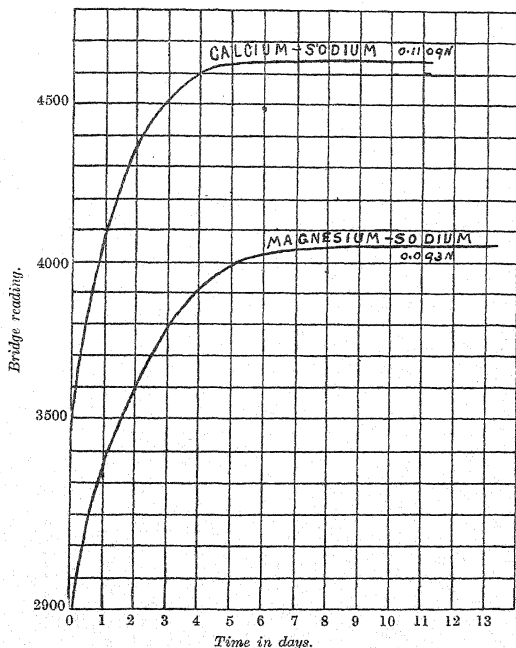
The cells were made up as described previously. The amounts of sucrose used to prevent osmosis were the same as those used with the potassium and sodium solutions of the same concentration. The concentrations of sucrose are probably too great in the case of the calcium solutions, since the calcium salt is less ionised in solution than the potassium salt, but no appreciable osmosis occurred. On the other hand, when the concentrations of sucrose were calculated from Sherrill's equations (*J. Amer. Chem. Soc.*, 1910, 32, 742), a considerable amount of osmosis occurred.

The rate at which equilibrium is reached is about as rapid as

in the case of the sodium-potassium cells. In some cases, the changes in concentration were followed by conductivity measurements. In Fig. 2 are given the changes of conductivity of a sodium-calcium and a sodium-magnesium cell respectively.

Time in days.	0.	1.	3.	4.	5.	6.	7.	8.	10.	12.
	Bridge-reading.									
Na-Ca .	3470	4082	—	4600	—	4635	—	4643	4635	—
Na-Mg .	2974	3358	3800	—	3994	—	4040	—	—	4060

FIG. 2.



From the curves and the above table, it will be readily seen that the rate of exchange of sodium and calcium ions is approxi-

ately equal to that of sodium and magnesium ions, and that a constant reading is obtained in about ten days.

The slight fall in the bridge-reading at the end of the experiment (Na-Ca) is probably due to the oxidation of the ferrocyanide.

#### *Method of Analysis.*

The analysis of the solutions of calcium and sodium ferrocyanides gave rise to considerable trouble, owing to the small volume (100 c.c.) which was available for analysis. The ferrocyanide solution was evaporated to dryness and decomposed with concentrated sulphuric acid. The mixed sulphates were dissolved in dilute hydrochloric acid, and the iron was removed as hydroxide with ammonia. The calcium was precipitated as oxalate and converted into oxide. Traces of iron were sometimes present in the oxide, which was on this account dissolved in hydrochloric acid and the iron precipitated. The calcium was then weighed as sulphate. The filtrate containing sodium sulphate was evaporated to dryness, traces of iron were removed, and the sodium was weighed as sulphate.

The results of the analyses are shown in table III, and it is found that

$$\frac{[\text{Ca}_1]}{[\text{Ca}_2]} = \frac{[\text{Na}_1]^2}{[\text{Na}_2]^2},$$

where the concentrations represent the total concentrations of the calcium and sodium atoms in the solution.

The ratio of the equilibrium concentrations of the calcium ferrocyanide on the two sides of the membrane is slightly higher than the ratio of the squares of the equilibrium concentrations of the sodium ferrocyanide, but the variations are of the same order as those due to errors of analysis.

The change in the degree of ionisation with concentration is known for potassium and calcium ferrocyanides, but not for sodium ferrocyanide.

	100α	
	K <sub>4</sub> Fe(CN) <sub>6</sub> .	Ca <sub>2</sub> Fe(CN) <sub>6</sub> .
(1) 0.05 Molar .....	48.6	22.1
(2) 0.025 Molar .....	53.1	23.5

(Noyes and Johnston, *J. Amer. Chem. Soc.*, 1909, **31**, 1010).

Similar figures have been obtained for calcium ferrocyanide in the course of this work.

Assuming that the sodium salt resembles potassium ferrocyanide, and that the ionisation of the mixed sodium and calcium salts is the same as in solutions of the pure salts with concentrations corre-

TABLE III.  
*Calcium-Sodium Cells.*

Cell.	Weight of		Na.	4Fe(CN) <sub>6</sub> .			$\frac{[Ca_1]}{[Ca_2]}$	$\frac{[Na_1]^2}{[Na_2]^2}$	$\frac{[Na_1]}{[Na_2]}$
	CaSO <sub>4</sub> .	Na <sub>2</sub> SO <sub>4</sub> .		I.	II.	III.			
1 a.....	0.1954	0.2276	0.0540	0.1213	0.1196	0.1185	1.265	1.248	1.117
b.....	0.1541	0.2037	0.0573	0.1026	0.1034	0.1029			
2 a.....	0.1673	0.2468	0.0615	0.1482	0.1495	0.1473	1.762	1.757	1.326
b.....	0.1188	0.2324	0.0349	0.1003	0.1030	0.1026			
3 a.....	0.1478	0.2064	0.0543	0.1269	0.1285	0.1236	1.368	1.332	1.154
b.....	0.1350	0.2235	0.0397	0.1026	0.1049	0.1023			
4 a.....	0.1775	0.2537	0.0652	0.1545	0.1534	0.1545	1.802	1.775	1.335
b.....	0.1231	0.2381	0.0362	0.1043	0.1042	0.1032			
5 a.....	0.2189	0.1319	0.1287	0.1973	0.2140	0.1995	1.547	1.495	1.223
b.....	0.2265	0.1595	0.0832	0.1393	0.1303	0.1420			



sponding with the ferrocyanogen-ion concentration (Arrhenius), it is possible to calculate the ratios of the calcium-ion concentration and the ratios of the squares of the sodium-ion concentrations on the two sides of the membrane. These are given in the table. The results (table IV) show that the relationship

$$\frac{[\text{Ca}_1^{++}]}{[\text{Ca}_2^{++}]} = \frac{[\text{Na}_1^+]^2}{[\text{Na}_2^+]^2}$$

does not hold so strictly as equation (1).

TABLE IV.

*Calcium-Sodium Cells.*

No.	$\frac{[\text{Ca}_1]}{[\text{Ca}_2]}$	$\frac{[\text{Na}_1]^2}{[\text{Na}_2]^2}$	$\frac{[\text{Ca}_1^{++}]}{[\text{Ca}_2^{++}]}$	$\frac{[\text{Na}_1^+]^2}{[\text{Na}_2^+]^2}$
1 .....	1.27	1.25	1.25	1.19
2 .....	1.76	1.76	1.68	1.58
3 .....	1.37	1.33	1.33	1.25
4 .....	1.80	1.78	1.73	1.61
5 .....	1.55	1.50	1.49	1.36

The activities of the ions of these two salts thus appear to be more nearly proportional to the molar concentrations than to the ionic concentrations.

Irregularities occurred in two of the cells. Cell 3, which was opened once during the experiment, shows that 2—3 per cent. of oxidation has taken place, and in cell 5 a change, due to osmosis, occurred. Neither of these changes appears to affect the ratio to any great extent.

In cell 5 it should be noted that the concentration of the calcium ferrocyanide is greater than that of the sodium ferrocyanide; in the other cells the reverse is the case.

*Amyl Alcohol Membrane.*

The results of some preliminary experiments on this membrane are given below.

*Materials.*—Amyl alcohol (b. p. 131.5°) was obtained by repeated fractionation of fusel oil through a six-bulb fractionating column. One sample of the alcohol was used throughout the work.

The lithium chloride was free from calcium, and was completely soluble in amyl alcohol. Its solution in water was neither acid nor alkaline. It was also analysed by conversion into lithium sulphate, followed by the estimation of the sulphate in this substance, as barium sulphate.

*Method.*—Aqueous solutions of lithium chloride were shaken with amyl alcohol in stoppered bottles in a thermostat kept at 25°, and when equilibrium had been reached, the two layers were analysed.

*Analysis.*—The aqueous solutions of lithium chloride were estimated volumetrically with *N*/10-silver nitrate, and the results were checked by analysis of the lithium as sulphate.

A known volume of the amyl alcohol layer was placed in a Jena-glass distilling flask, and the amyl alcohol distilled off. Water was added to the residue, and the solution titrated with silver nitrate.

The solutions containing the potassium and lithium chlorides were analysed according to the method employed by Gooch (*Proc. Amer. Acad.*, 22 N.S. 14, 177). A known volume of the aqueous solution was evaporated in the presence of 10 c.c. of amyl alcohol, and a little hydrochloric acid added to convert any lithium hydroxide into chloride. The lithium chloride dissolves in the amyl alcohol, and potassium chloride is left behind. The residue is collected and washed with hot amyl alcohol. The lithium is then estimated as sulphate, and the potassium chloride dissolved in water and estimated with silver nitrate. To check the results, the solution of the mixed chlorides was titrated directly with silver nitrate.

*Results.*—The concentrations of lithium chloride in the two layers are given in table V. The concentration of the lithium chloride in amyl alcohol diminishes rapidly with decrease in the concentration in the aqueous solution. The degree of ionisation of lithium chloride solutions cannot be given with any accuracy. The viscosity of the solutions is so great that allowance must be made in the derivation of the degree of ionisation from the conductivity results. Green (*loc. cit.*) has determined the

TABLE V.

*Distribution of Lithium Chloride between Amyl Alcohol and Water.\**

$\text{LiCl}_{\text{Aq.}}$ Total.	$[\text{LiCl}]_{\text{Am.}}$ Total.	100a.	$[\text{LiCl}]_{\text{Aq.}}$ undissociated.	$\frac{[\text{LiCl}]_{\text{Am.}}}{[\text{LiCl}]_{\text{Aq.}}}$
12.54N	1.735N	36.9	7.91N	0.0273
8.49	0.903	47.8	4.43	0.0428
7.77	0.683	50.5	3.85	0.0418
6.68	0.387	54.2	3.06	0.0366
5.00	0.1266	60.1	2.00	0.0277
3.14	0.0342	66.3	1.06	0.0255
3.00	0.0314	66.7	1.00	0.0262
2.71	0.0251	67.7	0.88	0.0268

\* In the calculation of the equilibrium constant a correction has been made for the degree of ionisation of the LiCl in the amyl alcohol solution.

viscosity and conductivity of solutions of lithium chloride over a wide range of concentration, and has corrected for the effect of viscosity by the addition of sucrose to the solution. The conductivity at infinite dilution was calculated over a wide range of viscosities; the degree of ionisation is obtained directly from the equation  $\alpha = \frac{\Lambda}{\Lambda_f}$ , where  $\Lambda$  is the conductivity of a solution of lithium chloride and  $\Lambda_f$  the conductivity at infinite dilution of a solution of lithium chloride containing sucrose, and with the same viscosity as the first solution. Washburn (*J. Amer. Chem. Soc.*, 1911, **33**, 1461) finds that the relation between the degree of ionisation, the conductivity, and the viscosity is given by the relation  $\alpha = \frac{\Lambda}{\Lambda_0} \left( \frac{f_0}{f} \right)^m$ , where  $f$  represents the fluidities and  $m = 0.94$ , but this holds only from 0—1.0*N*. For more concentrated solutions,  $m$  varies with the concentration. In table VI,  $m$  is given for the concentrations

TABLE VI.

*Degree of Ionisation of Concentrated Lithium Chloride Solutions.*

Normality.	$f$ .	$m$ .	$\lambda$ .	$100 \frac{\lambda}{\lambda_0} \left( \frac{f_0}{f} \right)^m$	$100\alpha(\text{Green})$ .
0.0	111.67	—	115.3	—	—
2.0	84.87	0.900	61.63	68.4	69.9
3.0	73.64	0.858	52.58	65.2	66.7
4.0	63.65	0.832	44.76	61.9	63.5
5.0	54.59	0.812	37.85	58.7	60.1
6.0	46.27	0.798	31.70	55.5	56.8
7.0	38.60	0.785	26.04	52.0	53.1
8.0	31.55	0.771	21.05	48.4	49.5
9.0	25.28	0.759	16.725	44.8	46.0
10.0	19.75	0.749	13.225	42.0	43.1
11.0	15.07	0.738	10.395	39.5	40.6
12.0	11.42	0.729	8.149	37.2	38.2

2—12*N*, and the value of  $m$  decreases from 0.90 to 0.73. The degree of ionisation calculated from the above equation and the data given by Green will be found in columns 5 and 6. The values are the same as those obtained by Green to within 1—2 per cent. The method of calculation is open to the objection that the lithium ion is probably hydrated in solution, and that the conductivity at infinite dilution,  $\Lambda_f$ , is given by lithium ions, which are probably hydrated to a different extent than is the case in a pure solution of lithium chloride with the same viscosity. The calculated values of the degree of ionisation will therefore be the more accurate for the more dilute solutions.

The values of  $\alpha$  in table VI, column 6, are used in tables V and VII. In table V, the amount of undissociated lithium

chloride (column 4) is calculated from these values of  $\alpha$ . From the figures in the last column, it will be seen that lithium chloride is associated in amyl alcohol solution to double molecules. A constant for  $\frac{[\text{LiCl}]_{\text{Am.}}}{[\text{LiCl}]_{\text{Aq.}}^2}$  is only obtained between 2*N* and 5*N*.

Above this concentration, the coefficient rises from 0.0277 to 0.0428, and then falls. The most probable cause of this deviation is discussed above, and it appears that the calculated concentrations of the undissociated molecules are too low.

The molar concentrations of the solutions of mixed chlorides in I. (p. 1315) and the corresponding equilibrium concentrations of lithium chloride in the amyl alcohol are given in table VII.

TABLE VII.

*Results with Amyl Alcohol Membrane.*

No.	Total KCl. I.	Total LiCl. I.	LiCl in amyl alcohol.	Total LiCl. II.	Undissociated LiCl		[Li'] × [Cl']	
					I.	II.	I.	II.
1	0.944	3.504	0.554	3.78	1.44	1.36	5.94	5.86
2	1.200	2.613	0.303	2.95	0.945	0.976	4.045	3.900
3	0.962	5.45	0.2236	5.80	2.39	2.46	11.02	11.17

From the amount of salt dissolved by the amyl alcohol, and the data in table V, the corresponding values of lithium chloride in II. are calculated and given in column 5. These figures represent the concentrations of lithium chloride in equilibrium with the solution of mixed chlorides in columns 1 and 2 across the amyl alcohol membrane. The ionic concentrations are obtained from Green's values for lithium chloride and from Kohlrausch and Grotrian's values for potassium chloride. The degree of ionisation for the higher concentrations of potassium chloride are obtained by extrapolation from the latter values. The degrees of ionisation of lithium and potassium chlorides are apparently very similar. The ionic concentrations of the solutions of the mixed chlorides are calculated on the assumption made in the case of the calcium-sodium ferrocyanide cells.

Cells 1, 2, and 3 show good agreement with the equations  $[\text{LiCl}]_1 = [\text{LiCl}]_2$  and  $[\text{Li}'] [\text{Cl}_1'] = [\text{Li}_2'] [\text{Cl}_2']$ . The agreement, which is better than would be expected, supports the values for the degree of ionisation of lithium chloride which were obtained by Green.

#### *Summary.*

Determinations have been made of the equilibrium concentrations of solutions of sodium and potassium ferrocyanides and

sodium and calcium ferrocyanides across a copper ferrocyanide membrane, and the results are in general agreement with Donnan's theory.

The following cells were investigated:

(a) I. Potassium ferrocyanide	Sodium ferrocyanide	II.
(b) I. Sodium ferrocyanide	Calcium ferrocyanide	II.
(c) I. Sodium ferrocyanide	Ammonium ferrocyanide	II.

The solutions in (a), (b), and (c) were in the neighbourhood of 0.025*N*.

A liquid membrane has been investigated; amyl alcohol was chosen as the most suitable solvent, and the electrolytes employed were potassium and lithium chlorides.

(d) I. Lithium chloride	Amyl alcohol	Lithium chloride	II.
Potassium chloride			

Lithium chloride gives rise to double molecules in amyl alcohol solution, and a constant is obtained for the partition-coefficient up to 5*N*.

So far as the preliminary experiments go, the equilibrium concentrations of the lithium and chlorine ions and the undissociated part of the electrolyte agree with Donnan's theory.

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### CXXIII.—*The Colouring Matter of the Red Pea Gall.*

By MAXIMILIAN NIERNSTEIN.

THE colours of oak galls are very varied and rich. They range from white and cream through all tints of yellow to deep orange, from pale green to a rich, dark hue, and through almost every shade of red, some being very beautiful and attractive. These red colours are generally ascribed to the presence of anthocyanins, which are supposed to be derived from the tannins present in galls (compare Gertz, "Studien öfver Anthocyans," 1906; Connold, "British Oak Galls," 1908; Küster, "Die Gallen der Pflanzen," 1911; Magnus, "Die Entstehung der Pflanzengallen," 1914). Our knowledge of the anthocyanins has been fundamentally increased

by the recent investigations of Wheldale, Willstätter, Everest, and others (compare Perkin and Everest, "The Natural Organic Colouring Matters," 1918). Their researches have conclusively proved that the anthocyanins are derived from the different flavones present in plants. This suggested an inquiry into the colouring matter of the so-called anthocyanin of the "red pea gall," frequently found on the leaves of different British oak trees, especially *Quercus pedunculata* when galled by *Dryophanta divisa*, Adler. It seemed reasonable to expect that the anthocyanin of this gall would in all probability be derived from cyanidin, the anthocyanin of quercetin, and, if so, it might furnish some evidence regarding the much discussed question as to the relationship between the pathological products produced by the gall and those normally present in the plant (compare Dekker, "Die Gerbstoffe," 1913). It was, incidentally, also thought possible that an anthocyanin derived from a gall might prove to be closely allied to quercetone or isoquercetone, both anthocyanin-like oxidation products of quercetin, described by Nierenstein and Wheldale (*Ber.*, 1911, 44, 3487) and Nierenstein (*T.*, 1915, 107, 869; 1917, 111, 4), as it was probable that the accelerated oxidative processes common to larvæ and imagines (compare Krogh, "The Respiratory Exchanges of Animals and Man," 1916), which, in addition to numerous inquilines, are present in large numbers in galls (compare Connold, *loc. cit.*; Küster, *loc. cit.*), would favour the production of an oxidation product, such as quercetone, and not that of a reduction product, such as cyanidin (compare Everest, *Proc. Roy. Soc.*, 1914, [B], 87, 444).

The investigation of the red colouring matter derived from the "red pea gall" has, however, to some extent proved disappointing. It was found that *dryophantin*, the name suggested for this pigment, was in no way allied either to the flavones or to the anthocyanins, but that it consisted of purpurogallin and two molecules of dextrose. On the other hand, it must be mentioned that purpurogallin has not previously been found in nature. *Dryophantin* is derived from pyrogallol, like gallotannin, and is therefore of pathological origin, like the latter. *Dryophantin*, however, cannot be regarded as an anthocyanin, and probably the same can be said of the other so-called anthocyanins derived from plant galls. It is therefore proposed to classify these red pigments in a new group of natural organic colouring matters, to which the name *gallorubrones* is assigned.

*Preparation of Dryophantin.*

The galls used in this investigation were collected in the vicinity of Bristol and East London during the months of August and September, 1913, 1915, 1917, and 1918, and care was taken to avoid admixtures with the different galls of the *Neuroterus* species frequently met with on the same leaves as the galls of *Dryophanta divisa*. In all, 94 grams of the galls were collected, and the dried material was powdered and extracted in a Soxhlet apparatus, at first with ether and subsequently with chloroform, so as to remove wax, chlorophyll, and the so-called gall-fats. The carefully dried powder was then again extracted in a Soxhlet apparatus with alcohol, which dissolved both the colouring matter and the tannins. The alcohol was distilled off in a vacuum, and the viscid residue redissolved in water. The cold aqueous solution, made up to 150 c.c., was shaken with 5 grams of fat-free caseinogen to remove the tannins (compare Körner and Nierenstein, *Chem. Zeit.*, 1911, 36, 31), filtered, and extracted with ether. The ether left on evaporation only traces of a tarry substance, apparently a by-product. The aqueous solution was evaporated under diminished pressure at about 55° (water-bath temperature), and the residue dissolved in boiling alcohol and filtered. The red alcoholic extract, after being evaporated to a small bulk, was poured into water, the mixture extracted several times with ether, and the small quantities of alcohol and ether present were removed from the aqueous liquid by prolonged heating on a boiling-water bath. The solution, on cooling, became semi-solid, owing to the separation of crystals; these were collected and washed repeatedly with ether and dilute alcohol. The deep red product obtained in this way was purified by several crystallisations from dilute, and finally absolute, alcohol. The air-dry substance was dried at 130° for analysis, without apparent loss of weight. The total amount of dryophantins thus obtained corresponded with about 4 grams, and there was no apparent difference if fresh or old material (about six months old) was used, which showed that there was apparently no deterioration on keeping.

Found: C=50.2, 50.4; H=5.5, 5.4.

$C_{28}H_{28}O_{15}$  requires C=50.6; H=5.2 per cent.

*Dryophantins* was obtained in deep red, glistening needles with a bronzy lustre. It was almost insoluble in cold alcohol, sparingly soluble in hot water, but fairly readily so in boiling methyl and ethyl alcohol, and in larger quantities of boiling acetone. It sintered at 216° and melted at 219–220° to a viscous liquid. The

addition of ferric chloride to its alcoholic solution produced a brick-red precipitate, and a similar precipitate, but slightly darker in colour, was also obtained by the addition of lead acetate. A trace of ammonia turned the alcoholic solution deep blue, which became red on acidification. These colour changes could be produced in an unlimited number of times in the same solution without affecting its sensitiveness to these reagents. Similar blue solutions were also obtained by the addition of sodium, potassium, or barium hydroxides to alcoholic solutions of dryophantin. In this connexion, it must be mentioned that similar colour changes are also given by purpurogallin itself (compare Wichelhaus, *Ber.*, 1872, 5, 848; Struve, *Annalen*, 1872, 163, 164; Hooker, *Ber.*, 1887, 20, 3259). On repeating these observations, it was found, however, that the colour changes are not so permanent in the case of purpurogallin as in the case of dryophantin.

#### *Hydrolysis of Dryophantin.*

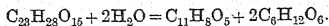
Experiments having shown that dryophantin was a glucoside, its decomposition with acid was studied in the following manner.

0.5246 Gram, dissolved in 550 c.c. of boiling water, was digested with 5 c.c. of sulphuric acid for two hours. A deep red, crystalline product commenced to separate, and more of it was deposited on cooling. This was collected in a Gooch crucible, washed with cold water so as to remove all traces of sulphuric acid, and dried at 160°. In this way, 0.1928 gram of purpurogallin was obtained.

Found: Purpurogallin = 36.7.

$C_{23}H_{28}O_{15}$  requires purpurogallin = 40.4 per cent.

The low value obtained for purpurogallin is due to its sparing solubility in water, and it was found that the filtrate recovered on hydrolysis of dryophantin to which had been added the washings of purpurogallin contained 2.2 per cent. of purpurogallin, when determined colorimetrically by Willstätter and Stoll's method for the estimation of small amounts of purpurogallin (*Annalen*, 1918, 416, 46). The total amount of purpurogallin from dryophantin corresponded, therefore, with 38.9 per cent., which is 1.5 per cent. below the theoretical if the hydrolysis of dryophantin is expressed as:



A second experiment gave 37.1 per cent. of purpurogallin gravimetrically and 1.9 per cent. colorimetrically, corresponding with 39.0 per cent. of purpurogallin, which is 1.4 per cent. below the theoretical.



The purpurogallin recovered from dryophantoin was recrystallised from glacial acetic acid, and had the correct melting point of 274—275° generally given for purpurogallin (Found: C=59·8; H=3·7. Calc.: C=60·0; H=3·6 per cent.). The acetyl derivative, which had been prepared by digesting with acetic anhydride, crystallised from alcohol in orange-yellow needles melting at 179—180°, and the melting point was not depressed after mixing with the tetra-acetyl derivative of purpurogallin (Found: C=59·2; H=4·7. Calc.: C=58·7; H=4·1 per cent.).

The filtrate from the first hydrolysis was quantitatively tested for dextrose by Fischer and Freudenberg's method (*Ber.*, 1912, 45, 915), and the dextrose estimated volumetrically in several portions of the hydrolysate by Bertrand's method (*Bull. Soc. chim.*, 1906, [iii], 35, 1286), as used by Geake and Nierenstein (*Ber.*, 1914, 47, 893) for the estimation of dextrose in gallotannin.

Found: Dextrose=62·8, 63·1, 63·0.

$C_{23}H_{28}O_{15}$  requires dextrose=63·3 per cent.

The filtrate of the second hydrolysis was prepared as in the experiment for the quantitative estimation of dextrose, and then concentrated to a small bulk. It was subsequently converted into dextrosazone, which crystallised from dilute alcohol in glistening, yellow needles melting at 203—204° (Found: N=15·8. Calc.: N=15·6 per cent.).

The author begs to acknowledge his indebtedness to the Government Grant Committee of the Royal Society for a grant from which much of the cost of the investigation was defrayed.

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CXXIV.—*The Effect of Salts on the Vapour Pressure and Degree of Dissociation of Acetic Acid in Solution. An Experimental Refutation of the Hypothesis that Neutral Salts Increase the Dissociation Constants of Weak Acids and Bases.*

By JAMES WILLIAM MCBAIN and JAMES KAM.

IN 1899 Arrhenius proposed a modification of his classical dissociation theory to the effect that salts increase the dissociation

constants of weak acids present with them in solution, as if either the water had acquired greater dissociating power or the salt itself was acting as a dissociating medium. The experimental evidence he adduced was the rate of inversion of sucrose by weak acids in the presence of salts.

Arrhenius's idea was very generally accepted and developed, particularly in the field of non-aqueous solutions; but in 1914 it was called in question by McBain and Coleman's re-interpretation of the direct experimental evidence. On recalculation of the data given by Arrhenius, in conformity with present-day conceptions of this reaction, they found that the supposed effect was entirely absent, thus reversing the significance of the experiments. In other words, the dissociation constant of weak acids is not affected by the presence of salts.

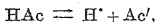
They followed this up by a review of all the available experimental evidence bearing on this subject, and they found that it supported only the simple form of the classical dissociation theory.

One isolated group of experiments was left outstanding, inasmuch as in this particular case the measurements were conflicting in their evidence; these were certain determinations of hydrogen ions by the method of electromotive force. The potential of the hydrogen electrode in solutions of acetic acid was greater than that predicted when sodium chloride was present, although this was not the case when sodium acetate was the added salt.

### (1) *Object of the Present Investigation.*

The present communication adduces a hitherto unsuspected but general effect of such salts as sodium chloride on undissociated acetic acid, which would account for the apparent results derived from the measurements of hydrogen electrode potential.

The equilibrium under discussion is



where HAc stands for a weak acid such as acetic acid. The potential of the hydrogen electrode in this solution is admittedly too great when sodium chloride is present. This has hitherto been interpreted as a real increase in acidity; in other words, a displacement of the equilibrium to the right—an enhancement of the dissociation constant itself.

The electrical potential of the hydrogen electrode, however, measures the product of the chemical potential and the concentration of the hydrogen ion. Instead of assuming that the increase in this product is due to increase in concentration, we here submit

experimental evidence for the alternative explanation that the other factor, the chemical potential, has been enhanced.

If the concentration of the hydrogen ion has remained unaltered, but its chemical potential or reactivity has been increased, it is necessary for the continuance of equilibrium that the chemical potential or reactivity of the substance on the left-hand side of the chemical equation should likewise have increased. Such increase in reactivity or potential of undissociated acetic acid in the solution must be accompanied by a parallel increase in the partial pressure of acetic acid in the vapour phase.

This is open to direct experimental test, and we find that a remarkable increase is actually exhibited, fully accounting for the electromotive force data observed. This removes the last evidence in favour of Arrhenius's proposed modification of his classical dissociation theory. The effect here discovered has to be taken into account in most determinations of electromotive force.

## (2) *The Experimental Method.*

The simple experimental method adopted was the distillation of aqueous solutions of acetic acid with and without addition of various salts.

Pipettes, burettes, and measuring flasks were carefully calibrated. The distillations were carried out in a flask of fused silica of about 1500 c.c. capacity, heated directly by contact with a large Bunsen flame. The neck and upper half of the flask were covered with a lagging of magnesia and asbestos, so as to avoid as much as possible fractional distillation in the flask. The distance between burner and flask was kept constant through all distillations, as was also the flame itself.

The quantity of distilling liquid was each time 1000 c.c., and the distillate was collected in four to five fractions of about 75 c.c. each. After each fraction, the distillation was quickly interrupted for the abstraction of a similar quantity of about 75 c.c. from the residue in the flask; the first residue was abstracted as soon as the liquid began to boil and just previous to the collection of the first fraction of the distillate.

The residues were left to cool in glass-stoppered bottles, vaseline being used on the stoppers to prevent ingress of carbon dioxide from the air.

Samples of 20 c.c. of each of the distillates and residues were titrated against standard solutions of sodium hydroxide of approximately equal strength, with phenolphthalein as indicator; the usual precautions were taken to avoid the vitiating effect of carbonic acid. Thus for each distillate the ratio  $R_2$  could be

determined between the concentrations of acetic acid in that distillate and the mean concentration of acid in the residue in the flask before and after.

Thus the ratio  $R_2$  was determined for solutions of acetic acid of concentrations varying from 0.05 to 0.5*N*. It appeared that, at least between these limits,  $R_2$  increases only very slightly with the concentration, as is apparent from the curve No. I of Fig. 1, which shows the value of  $R_2$  plotted against the acid concentrations.

The same operations were repeated with solutions of sodium, potassium, and lithium chlorides, potassium thiocyanate, potassium nitrate, sodium sulphate, and sodium acetate in 0.05 to 0.4*N*-solutions of acetic acid. The concentration of the salts was determined by careful evaporation of 20 c.c. of each residue in a porcelain evaporating dish in a hot-air oven at temperatures depending on the nature of the salt in question. The acetic acid was titrated as before, in distillate and residue, to obtain the ratio  $R_1$  of the concentration.

The values of the ratios  $R_1$  are dependent on the concentration of the salts, but they are independent of the concentration of acetic acid. Sodium acetate differs from the other salts investigated in that it has scarcely any effect on the distillation of acetic acid.

In this manner, values of  $R_2$  derived from a very large number of distillations of solutions of pure acetic acid became the standard of comparison for a number of distillations of acetic acid containing added salts.

The expression  $100 \frac{(R_1 - R_2)}{R_2}$  gives the percentage increase of the ratio  $R_1$  caused by the addition of salt. The experimental data here presented comprise well above one hundred such determinations.

### (3) *Method of Calculation of the Distillation Data.*

Distillation was selected for the measurement of the partial vapour pressure of acetic acid merely for the sake of convenience and accuracy. It must be borne in mind that the composition of the distillate shows only the relative proportion of acetic acid and water vapour in the vapour phase above the solution. What is required is the absolute magnitude of the partial vapour pressure of acetic acid at a definite temperature, say 100°. The polymerisation of the acetic acid vapour may be neglected for the present purpose, since it amounts to only a few per cent. at these low

partial pressures. Even this slight effect is largely eliminated in comparing  $R_1$  with  $R_2$ .

Ordinary variations in barometric pressure and the concomitant alterations in boiling point have no appreciable influence on the composition of the distillate. Hence, all the distillations may without error be regarded as having been in effect carried out at  $100^\circ$ , even where much salt has been added.

In order to obtain the absolute instead of the relative magnitude of the partial pressure of acetic acid in the vapour distilling over at  $100^\circ$ , the actual partial pressure of the water has to be evaluated. Now, the partial pressure of the water, which in pure water was 760 mm., has been diminished by two effects, for which allowance has to be made.

The first correction may be termed the "osmotic correction." The vapour pressure of the solvent has been reduced in familiar fashion through the osmotic activity of the substance in solution. Hence, in all cases the observed concentration of the acetic acid in the distillate must be diminished accordingly before use. This is readily done with sufficient accuracy for the present purpose by taking the lowering of vapour pressure of the solvent to be 1.80 per cent. per mol. of total solute (ions and undissociated acid and salt).

The second correction is the "volatility correction." It results from the effect of the appreciable partial pressure of the acetic acid in lowering the pressure at which the water actually distills over, instead of this occurring at a partial pressure of water vapour equal to 760 mm. Here again, then, in order to base the relative magnitude of the partial pressure of acetic acid on the constant value of 760 mm. for that of water vapour throughout, the volatility correction has to be applied so as to diminish the observed concentration of the acetic acid in the distillate accordingly. This consists in the reduction of the latter by 0.12 per cent. for a 0.1*N*-solution of acetic acid, and taking this correction as proportional to the concentration of the acetic acid in the distillate. Since the acetic acid was at most  $N/2$ , this correction in no case exceeded 0.6 per cent.

A third and final correction had to be made, this time in the apparent composition of the solution undergoing distillation. This is the "correction for dissociation" of the acetic acid in the solution. The actual ratios measured were those between the concentrations of distillates and the corresponding solutions in the distilling flask (the "residues"). What is required is the ratio based on the actual concentration of undissociated acetic acid in the flask. In the case of solutions containing only acetic acid,

this consisted simply in subtracting the known amount of dissociated acetic acid from the total concentration of acetic acid in the flask. The dissociation constant of acetic acid was taken to be  $1.11 \times 10^{-5}$  at  $100^\circ$ .

The correction for dissociation involves much calculation where salt is present, since in order to determine the actual concentration of undissociated acetic acid, it is necessary to calculate the amounts of the various ions and undissociated salts present, including those formed by metathesis. For example, with common salt the following molecular species were present:  $H^+$ ,  $Ac'$ ,  $Na^+$ ,  $Cl'$ ,  $HAc$ ,  $HCl$ ,  $NaCl$ , and  $NaAc$ .

This was done by Arrhenius's method, which is based on the principle of isohydrism (*loc. cit.*), and agrees with the method of Sherrill (*J. Amer. Chem. Soc.*, 1910, **32**, 741). The calculation is laborious and involves successive approximations. Fortunately, the exact degree of dissociation of the various salts has but little influence on the results, since the really important values appear in both numerator and denominator of Arrhenius's equations; conductivity data at the ordinary temperature could therefore be employed failing the existence of such at higher temperatures and concentrations. Indeed, the calculation for solutions of one salt in acetic acid might have been applied to the case of any other salt of the same concentrations, except, of course, in the case of sodium acetate. The effect is chiefly dependent on the relative concentration of acid and added salts.

#### (4) *The Distillation of Solutions of Pure Acetic Acid.*

Following the method already described, fifteen distillations were carried out with  $N/20$ - to  $N/2$ -solutions of acetic acid involving more than seventy determinations. The object in view was to determine the ratio  $R_2$ , that is, the ratio, concentration of acid in distillate to concentration of acid in residue.

Thus

$$R_2 = \frac{C_d}{C_r},$$

$C_d$  being the concentration of the distillate,  $C_r$  being the mean value of the concentrations of the residue before and after the separation of the distillate.

The experimental evidence is summarised in table I. For any one concentration, the results agreed to within 1 per cent. The values of  $R_2$  were corrected as described in Section (3) above, and they increase by only about 1 per cent. over the whole range of concentration. The relative concentration of double molecules, which has not been allowed for, changes from about 5 to 3 per cent. over this same range.

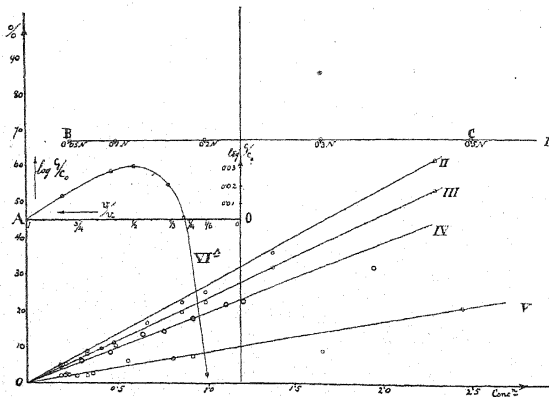
TABLE I. (Curve I.)

*Ratio of Concentration in Distillate and Residues in Aqueous Acetic Acid.*

Concentration of acid in flask.	$R_2$ (uncorrected).	$R_2$ (corrected).
$N/20$	0.662	0.671
$N/10$	0.666	0.671
$N/5$	0.673	0.674
$N/3$	0.680	0.677
$N/2$	0.685	0.678

The corrected values of  $R_2$  increase very slowly indeed. Plotting them against the concentrations, we obtain a straight line (Curve I in Fig. 1).

FIG. 1.



- I.  $\text{CH}_3\cdot\text{CO}_2\text{H}$ , corr. ( $B=0.671$ ;  $C=0.678$ ).  
 II.  $\text{NaCl}$ , uncorr. Percentage increase due to salt.  
 III.  $\text{NaCl}$ , corr. " " " "  
 IV.  $\text{KCl}$ , " " " "  
 V.  $\text{KCNS}$ , " " " "

$$\text{VI}^A. \text{Curve: } \log \frac{C_1}{C_0} = \frac{1}{2.3026} \left[ \left( 1 - R_2 \right) \cdot \log \frac{v_0}{v_1} \cdot 2.3026 + R_2 \cdot K \cdot \left\{ \frac{v_1 - v}{v_1 \cdot v_0} \right\} \right]$$

$A0 = v_0 = 1.$

*Ratios of acetic acid in distillate and residue with and without added salts.*

The corrections for volatility and osmotic effect can be taken from graphs; for example, in the case of  $N/20$ -acetic acid, they

amount to  $-0.06$  and  $-0.09$  per cent. respectively. The third correction for degree of dissociation of the acetic acid is here  $1.50$  per cent. Thus the total correction in this case is an increase of  $1.35$  per cent. on the observed ratio  $R_2=0.662$ . Hence we obtain

$$R_2 \text{ (corrected)} = 0.662 \times 1.0135 = 0.671.$$

This value is smaller than the one arrived at by Lord Rayleigh (*Phil. Mag.*, 1902, [vi], 4, 535),  $R_2=0.73$ . Corrected, it reduces slightly to  $0.725$ , which is still considerably greater (the reduction in this case being caused by the method of calculation of  $R_2$  from the residues). The discrepancy is, however, probably due to the different manner of heating. Lord Rayleigh kept the neck and upper part of the distilling flask hotter than the boiling liquid in order to prevent condensation. We found, however, that this involved the quantitative evaporation of drops splashing up from the boiling liquid, which produces the same error as if they had splashed directly into the distillate. It was for this reason that we relied on good heat insulation and fairly rapid distillation.

*Note on the Calculation of the Composition of the Residues at any given Stage of the Distillation of Acetic Acid.*

Following Lord Rayleigh (*loc. cit.*), but using concentration of residues expressed in mols. per litre,

$$\frac{C_0}{C_1} = \left( \frac{V_0}{V_1} \right)^{R_2 - 1},$$

where  $C_0$  and  $C_1$  are the concentrations and  $V_0$  and  $V_1$  the volumes in the distilling flask before and after the distillation.

For example, for  $R_2=0.671$  and  $\frac{C_0}{C_1} = \frac{1}{2}$ ,  $\frac{V_0}{V_1} = 8.221$ . Hence, in order to double the concentration of the residual acid solution in the flask,  $\frac{7.221}{8.221} = 0.878$ , or almost 88 per cent. of the volume of the solution must be distilled over. For  $R_2=0.73$  (Rayleigh's value in  $N/10$ -solution), this quantity would amount to 92 per cent.

Again, if 40 per cent. of the original volume of solution is distilled off, that is, if  $V_1 = 0.6 V_0$ ,  $\frac{C_1}{C_0} = 1.183$ , which means that the concentration of the residue will have increased by 18.3 per cent.

(5) *The Experimental Data for Added Salts.*

Having determined the ratios  $R_2$  for solutions of acetic acid, the corresponding ratios,  $R_1$ , were obtained in exactly the same manner, but with a salt added to the solution.



The salts used were the purest obtainable in 1913, and are named in Section (2) (above).

The distillates were in each case tested for traces of the stronger acid formed by metathesis, but these were found to be negligible. The corrections were calculated and applied in the same manner as before, except that the acetic acid destroyed by metathesis was calculated according to Arrhenius's principle of isohydrism (*Zeitsch. physikal. Chem.*, 1899, **30**, 208).

The results are summarised in tables II—VIII, which require no further explanation, except to note that in tables II and VII space is saved by averaging the figures for all the values obtained over certain ranges of concentration. The number of experimental values so averaged is given in the last column.

With the exception of sodium acetate, all these salts cause a remarkable increase of the ratio  $\frac{C_d}{C_r}$ , and sodium chloride shows this increase more than any other of the salts investigated. Sodium acetate, on the other hand, appears to have no appreciable effect even in 1.0*N*-solution.

#### TABLES II.—VIII.

*Ratios  $R_1$  of Concentration of Distillates and Residues of Aqueous Acetic Acid with added Salts, and Increase thereof over  $R_2$  of Table I.*

TABLE II. (Curves II. and III.). *Sodium Chloride.*

HAc.	Salt.	$R_1$ .	$R_2$ .	$R_1$ (corr.).	$R_2$ (corr.).	$100 \left[ \frac{R_1 - R_2}{R_2} \right]$	Expts.
0.1—0.2	(0.12)	0.688	0.669	0.690	0.673	2.6	7
0.1—0.3	(0.21)	0.708	0.671	0.710	0.673	5.4	16
0.1—0.3	(0.29)	0.721	0.672	0.716	0.673	6.6	15
0.1—0.3	(0.41)	0.742	0.671	0.721	0.673	9.6	4
0.13	0.661	0.790	0.668	0.715	0.671	16.9	1
0.076	1.04	0.830	0.663	0.820	0.671	22.2	1
0.078	1.38	0.904	0.664	0.885	0.671	32.1	1
0.077	2.30	1.076	0.664	1.033	0.671	53.9	1

TABLE III. (Curve IV., Fig. 1). *Potassium Chloride.*

0.22	0.2—0.3	0.7146	0.673	0.7111	0.674	5.55	4
0.2540	0.4673	0.7389	0.675	0.7309	0.675	8.20	1
0.2157	(0.70)	0.7741	0.673	0.759	0.674	13.55	2
0.2053	0.9228	0.8121	0.673	0.7930	0.674	17.70	1
0.22	1.17	0.8383	0.673	0.8133	0.674	21.55	2
0.2194	1.953	0.9363	0.673	0.8872	0.674	31.60	1

TABLE IV. (Curve V., Fig. 1). *Potassium Thiocyanate.*

0.2—0.23	0.2—0.34	0.6900	0.673	0.6868	0.674	1.90	6
0.2673	0.5590	0.7297	0.675	0.7181	0.675	6.40	1
0.2366	1.663	0.7693	0.674	0.7343	0.674	8.90	1
0.2595	2.451	0.8710	0.675	0.8112	0.675	20.10	1

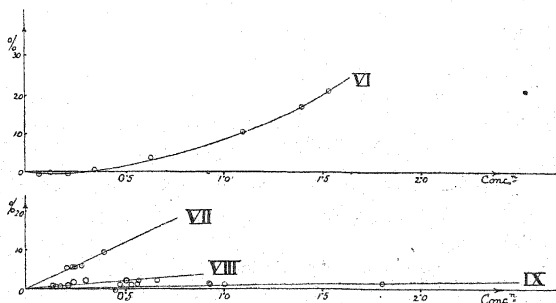
TABLE V. (Curve VI., Fig. 2). *Sodium Sulphate.*

HAc.	Salt.	$R_1$	$R_2$	$R_1$ (corr.)	$R_2$ (corr.)	$100 \left[ \frac{R_1 - R_2}{R_2} \right]$	Expts.
0.22	(0.07)	0.669	0.673	0.669	0.674	-0.7	5
0.22	(0.13)	0.674	0.673	0.673	0.674	-0.2	8
0.25	(0.22)	0.674	0.675	0.671	0.674	-0.4	7
0.25	(0.35)	0.683	0.675	0.678	0.674	+0.5	5
0.27	(0.61)	0.710	0.677	0.700	0.675	+3.8	2
0.29	1.10	0.762	0.678	0.743	0.675	+10.0	1
0.21	1.40	0.807	0.673	0.786	0.674	+16.6	1
0.22	1.54	0.839	0.673	0.813	0.674	+20.6	1

TABLE VI. (Curve VII., Fig. 2). *Lithium Chloride.*

0.2—0.22	0.2—0.25	0.7143	0.673	0.7116	0.674	5.57	3
0.2269	0.2799	0.7188	0.673	0.7147	0.674	6.00	1
0.2469	0.3930	0.7450	0.674	0.7375	0.674	9.40	1

FIG. 2.



VI.  $\text{Na}_2\text{SO}_4$ , corr.  
VII.  $\text{LiCl}$  „

VIII.  $\text{KNO}_3$ , corr.  
IX.  $\text{NaCH}_3\text{CO}_2$ , corr.

Percentage increase in ratios of acetic acid in distillate and residue due to added salts.

TABLE VII. (Curve VIII., Fig. 2). *Potassium Nitrate.*

0.21	0.22	0.6944	0.673	0.6940	0.674	1.13	2
0.24	0.3—0.5	0.7198	0.674	0.7110	0.674	2.32	2

TABLE VIII. (Curve IX., Fig. 2). *Sodium Acetate.*

0.11	(0.14)	0.6822	0.667	0.6769	0.671	0.8	3
0.1—0.23	0.4—0.67	0.6948	0.671	0.6799	0.673	0.9	7
0.1—0.28	0.9—1.1	0.7001	0.673	0.6799	0.673	1.3	3
0.2900	1.810	0.7244	0.678	0.6834	0.675	1.3	1

The increase of  $R_1$ , the relative concentration of the distillate, for the same solution of acetic acid, that is, the expression

$100\left(\frac{R_1 - R_2}{R_2}\right)$  amounted to no less than 62 per cent. (observed) in the case of 2.3*N*-sodium chloride.

The increase for most salts seems proportional to the concentration of the salt and independent of the concentration of acetic acid.

Curves II—V of Fig. 1 and VI of Fig. 2 show this percentage increase plotted against the concentrations, and they point convincingly towards a straight line function between these two values. Sodium sulphate differs from all the other salts in that the experimental evidence shows a slightly negative effect at lower concentrations, up to about 0.3*N*.

*Note on the Calculation of Residues in the Presence of Salts which exhibit a Straight Line Function of the Ratio Increase.*

The calculation is similar to the one for the pure acid solution, but we must introduce the functional relation of  $R_1$  with regard to the concentration of the salt.

We have found experimentally for all salts except the sulphate and acetate

$$100\left(\frac{R_1 - R_2}{R_2}\right) = 100K\rho \text{ or } R_1 = R_2(K\rho + 1),$$

in which  $\rho$  is the concentration of the salt and  $K$  is a constant. Hence  $R_1 = R_2\left(\frac{K}{V} + 1\right)$ , where  $V$  is the volume in litres containing 1 mol. of salt.

If there are  $y$  mols. of acetic acid in  $V$  litres of the solution in the flask, and a quantity  $dv$  of the solution containing  $dy$  of the acetic acid distils over, we may set the concentration of the distillate equal to  $\frac{dy}{dV} = R_1 \frac{y}{V} = R_2\left(\frac{K}{V} + 1\right) \frac{y}{V}$ . Since  $c = \frac{y}{V}$ , and by differentiation  $\frac{dc}{c} = \frac{dy}{y} - \frac{dV}{V}$ ,  $\frac{dy}{dV} = c + V \frac{dc}{dV} = R_2\left(\frac{K}{V} + 1\right)c$ , or  $\frac{dc}{c} = \left(\frac{R_2 K}{V^2} - \frac{R_2 - 1}{V}\right)dV$ .

Integrating,

$$\ln \frac{c_0}{c_1} = R_2 K \left( \frac{V_0 - V_1}{V_0 \cdot V_1} \right) + (R_2 - 1) \ln \frac{V_0}{V_1},$$

or

$$\log \frac{C_1}{C_0} = \frac{1}{2.303} \left[ (1 - R_2) \left( \log \frac{V_0}{V_1} \right) 2.303 + R_2 K \left\{ \frac{V_1 - V_0}{V_1 \cdot V_0} \right\} \right],$$

where  $C_0$  and  $C_1$  are the concentrations and  $V_0$  and  $V_1$  the volumes in the distilling flask before and after distillation.

An alternative formula deducible in the same way is

$$\log \frac{y_0}{y_1} = \frac{R_2}{2.303} \left[ 2.303 \log \frac{V_0}{V_1} - K \left\{ \frac{V_0 - V_1}{V_0 \cdot V_1} \right\} \right].$$

Either of these expressions can be used to calculate the concentration of the acetic acid in the distilling flask if the initial value of the salt concentration and either its increase or the relative volume of the residual solution are given. They contain two constants.  $100K$  is the one which is peculiar to the added salt, and it is simply the percentage increase by 1.0*N*-salt. The other,  $R_2$ , is the ratio of acetic acid in distillate and residue for the same solution in the absence of salt. It is convenient to express  $V_1$  as a fraction of  $V_0$ , the volume at the beginning of the distillation containing 1 mol. of salt; but the initial concentration of salt in mols. per litre =  $\frac{1}{V_0}$ .

Inspection of the equations show that they are identical with that deduced above for solutions of pure acetic acid, except for the correcting factor  $R_2 K \left( \frac{V_0 - V_1}{V_0 \cdot V_1} \right)$ . This factor, of course, disappears for large values of  $V_0$ , that is, for very low concentration of added salt. Conversely, for very high concentrations of salt it is predominant, as is evident from the consideration that for, say, 2.6*N*-potassium chloride, no separation takes place, owing to the concentration of acetic acid in the distillate having been so raised as to equal that of the residue. Above such concentrations, the residue becomes weaker instead of stronger.

The general behaviour of a distillation is shown graphically in curve VI<sub>A</sub> of Fig. 1, which assumes that 1.0*N*-sodium chloride was initially present ( $V_0=1$ ). As the distillation proceeds, the salt accumulates, and the concentration of acetic acid in the residue slowly rises to a maximum where 50 per cent. of the liquid has distilled over ( $V_1=0.5$ ). At this point,  $\log \frac{C_1}{C_0} = 0.03$ , whence the increase of concentration is 7.2 per cent. At  $V_1=0.27$ , when 73 per cent. has been distilled over, the concentration of the acid is again the same as it was before the distillation. Beyond this point, the value for  $\log \frac{C_1}{C_0}$  assumes rapidly negative values,

owing to the high concentration of salt in the residue.

The general equation may be tested by one of our experimental results. Taking the last pair of values in table III for potassium chloride, 1.0*N*-potassium chloride increases the ratio of acetic acid by 18.5 per cent., hence  $K=0.185$ . Further,  $R_2=0.674$ ,

$V_1 = \frac{1.128}{1.953} V_0$ ,  $V_0 = \frac{1}{1.128}$ . These values inserted in the equation lead to the prediction that  $C_1 = 1.078C_0$ . Experimentally,  $C_0$  was  $0.2118N$  (less 1 per cent. for metathesis) and  $C_1$  after distillation  $0.2194N$  (plus 5 per cent. for the three corrections). Hence  $C_1 = \frac{0.230}{0.210} C_0 = 1.095C_0$ . In general, the concentrations observed appear to agree with the predicted values within about 2 per cent.

To sum up, the process of concentration or separation of the constituents of a binary mixture by means of distillation may thus be considerably accelerated or retarded by the addition of a salt, and will largely depend on the values of the constants  $R_2$  and  $K$ , that is, on the nature of the mixture and of the added salt.

#### (6) *Discussion of the Results.*

The remarkable effect of a salt on the partial vapour pressure of acetic acid must be evident from the preceding. Comparing the slopes of the various graphs showing the relationship between salt concentration and percentage ratio increase, it appears that the effect is greatest for the chlorides of lithium, sodium, and potassium, and least for sodium acetate. The effect is in all cases independent of the concentration of the acetic acid.

The increase of the concentration of the residue in the flask for acetic acid in aqueous solution during the distillation, not very rapid in itself, is still less if salt is also present. At a concentration of  $2.3N$ -sodium chloride, the residue becomes weaker; in other words, the vapour phase in the flask contains more acetic acid than the liquid from which it originates.

For sodium sulphate up to about  $0.35N$ , the experimental evidence for the ratio increase seems somewhat complicated. If anything, there is a negative effect, as the course of curve VI in Fig. 2 indicates. Beyond  $0.35N$ , the effect is decidedly positive. Between  $0.35N$  and  $1.1N$ , the graph is practically a straight line, but beyond  $1.1N$  its slope appears to increase until, at  $1.55N$ , the limit of solubility is approached.

Sodium acetate up to  $1.8N$  shows only a very slight effect.

Although the effect of the cation is undeniable (note, for example, the greater slope of the ratio increase for sodium chloride as compared with the one for potassium chloride), the influence of the anion seems to be the predominating factor. The series sodium acetate, potassium nitrate, potassium thiocyanate, sodium sulphate, potassium chloride, lithium chloride, sodium chloride, shows the increase in a progressive degree. It is evident that this order is not that of the Hofmeister or lyotropic series.

It is well known that there is a general qualitative similarity between the effect of neutral salts on such various phenomena as solubilities of gases and non-electrolytes, surface tension, compressibility, maximum density of water, viscosity, dielectric constant, imbibition and gelatinisation of gels, and increase or decrease of rate of catalysis. The explanation of this undoubted parallelism is wholly unknown, and in each individual case there are pronounced exceptions. In the present instance, the exceptions are the acetate and the sulphate, although they may be paralleled by certain cases of catalysis. Possibly in the case of the sulphate our correction for metathesis (formation of  $\text{HSO}_4'$ ) has not been sufficiently great. The effects are reconcilable with a solvate form of the dissociation theory.

With regard to the main thesis of this paper, it has now been proved that the reactivity of the undissociated acetic acid is increased by addition of such salts as sodium chloride. A  $0.2N$ -solution is affected to the extent of 5.5 per cent. by  $0.2N$ -sodium chloride. It was pointed out in the earlier paper (*loc. cit.*) that Walpole's measurements of electromotive force for this particular case gave a result for the hydrogen ion which was 7 or 8 per cent. too high. These two effects, 5.5 and 7 or 8 per cent., are equal within the experimental error, and thus the effect on the dissociation constant deduced for acetic acid cancels out and leaves that constant unchanged by the presence of the salt.

Thus the electromotive force data may be regarded as agreeing with all the other data bearing on this subject, and the experimental evidence all points to the conclusion that the dissociation constants of weak substances are not appreciably affected by the addition of salts. One point we have not investigated, namely, the effect of salts on the chemical potential of the acetate ion.

#### *Summary.*

(1) It is shown experimentally that many salts enhance the partial vapour pressure of acetic acid in aqueous solution by very appreciable amounts. In the case of  $2.3N$ -sodium chloride, the increase amounts to no less than 62 per cent.

(2) Since this partial pressure is a measure of the reactivity of the undissociated acid in the solution, the undissociated acid must be regarded as exhibiting enhanced chemical potential in the presence of such salts. This is parallel with the available data for the effect of such salts on the measurement of hydrogen ion by electromotive force. The enhancement is thus discovered to be operative on both sides of the chemical equation, and hence to leave the dissociation constant of acetic acid sensibly unaltered.

These experiments remove the only remaining evidence (apart from the ambiguous behaviour of certain insufficiently investigated colloids) for the view that salts might have been regarded as increasing the strength of weak acids.

(3) Whereas a number of salts increase the partial pressure of acetic acid to an extent proportional to the concentration, sodium sulphate exhibits a more complicated behaviour, whilst sodium acetate has only a very slight effect. All electromotive force data on weak acids in the presence of salts other than sodium acetate require to be corrected for the effects here described.

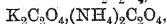
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## CXXV.—Some Ternary Systems containing Alkali Oxalates and Water.

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THERE has been considerable discussion at various times regarding the alleged formation of certain double oxalates of the alkali metals. Wenzel is quoted by some early writers as maintaining the existence of the double salts  $K_2C_2O_4 \cdot Na_2C_2O_4$  and



but Rammelsberg (*Ann. Phys. Chem.*, 1850, [ii], 79, 562) has thrown doubt on the one case and Souhay and Lenssen (*Annalen*, 1856, 99, 31) on the other.

Foote and Andrew (*Amer. Chem. J.*, 1905, 34, 164) drew the same conclusions as Rammelsberg and Souhay and Lenssen, and claimed to have shown that these double oxalates do not exist at 25° in the solid state. They state that the solid monohydrates of potassium and ammonium oxalates remain in equilibrium with a common saturated solution, and that the same holds for anhydrous sodium and hydrated potassium oxalates. A few years later, Barbier (*Bull. Soc. chim.*, 1908, [iv], 3, 725) described a double oxalate of potassium and ammonium, stating that it might readily be formed by adding a concentrated solution of potassium oxalate to a saturated solution of ammonium carbonate. The analysis he quotes points to a pure, 1:1, anhydrous double salt.

None of the authors mentioned made complete investigations by the solubility method. Foote and Andrew (*loc. cit.*) obtained a few solubility figures, but to determine the solid phases present they relied on a general principle laid down in a previous paper (*ibid.*, p. 153) that when two salts are mixed in varying proportions and treated with water at a constant temperature, the residue of undissolved solid remains constant in composition and the solution varies if a pure double salt is present, whilst, on the other hand, the residue varies and the solution remains constant in composition when a mere mixture of the two single salts is present. This rule is liable to mislead, if only because it does not take into account the possibility of the formation of mixed crystals (solid solutions).

It has seemed worth while, therefore, to apply the solubility method more fully to some of these ternary systems of alkali oxalates in water. Knowledge of the solid phases present has been obtained by the customary graphic method of plotting in a triangular diagram the percentage compositions of pure solution and of the moist solid (or "residue") in equilibrium with it, and extrapolating the straight line joining the two points to the composition of the pure solid uncontaminated with adhering solution. The systems investigated are those containing potassium, sodium, and ammonium oxalates, in pairs, with water. The solid phases of the individual salts stable at these temperatures with their own aqueous solutions are, respectively,  $K_2C_2O_4 \cdot H_2O$ ,  $(NH_4)_2C_2O_4 \cdot H_2O$ , and  $Na_2C_2O_4$ .

#### EXPERIMENTAL.

##### I. System: $K_2C_2O_4$ -( $NH_4$ ) $_2C_2O_4$ - $H_2O$ at 25° and 50°.

The system potassium oxalate, ammonium oxalate, and water has been examined at 25° and 50°, and the figures obtained are given in tables I and II, respectively, and plotted in Fig. 1.

Suitable mixtures of the salts (monohydrates) and water were heated in bottles, which were sealed and placed in a thermostat, in which they were continuously rotated for about forty-eight hours. Undissolved solid was allowed to settle, and clear solution drawn into a pipette through a small plug of cotton wool held in rubber tubing. A known weight was diluted to a suitable volume for subsequent analyses. Residues were obtained by pouring solution and suspended solid on to a Buchner funnel, drawing the solution through rapidly by means of a pump, but disconnecting the pump before more than a very small amount of air had been



drawn through the moist solid. A slight loss of water vapour at  $50^\circ$  is inevitable, but with rapid working it can be made almost negligible.

Total oxalate was determined by titration of a fraction of the stock solution with standard potassium permanganate, ammonium by distillation with alkali and absorption of ammonia in standard acid, and potassium by difference. Concentrations have been expressed in percentages by weight, but as densities have been determined in all cases, figures for concentrations in other terms are readily obtainable.

TABLE I.

25°.

No.	Density.	Percentage composition of solution or residue (R).			Solid phases.
		$K_2C_2O_4$ .	$(NH_4)_2C_2O_4$ .	$H_2O$ .	
1	1.021	—	5.01	95.0	$(NH_4)_2C_2O_4 \cdot H_2O$ .
2	1.040	2.67	4.72	92.6	Solid solution of $K_2C_2O_4 \cdot H_2O$ in $(NH_4)_2C_2O_4 \cdot H_2O$ .
R 2	—	0.44	81.3	18.3	"
3	1.058	4.32	4.48	91.2	"
R 3	—	2.41	56.4	41.2	"
4	1.068	6.51	4.38	89.1	"
R 4	—	2.75	61.1	36.1	"
5	1.087	9.48	4.16	86.4	"
R 5	—	2.62	72.3	25.1	"
6	1.107	12.10	4.01	83.9	"
7	1.124	14.18	3.78	81.0	"
8	1.128	15.37	3.68	80.9	"
9	1.137	16.54	3.57	79.9	"
R 9	—	2.14	80.4	17.2	"
10	1.166	19.39	3.32	77.3	"
R 10	—	4.37	76.4	19.2	"
11	1.185	21.9	3.10	75.0	"
R 11	—	6.70	76.2	19.2	"
12	1.204	24.3	2.90	72.8	"
R 12	—	13.4	61.9	24.7	"
13	1.217	25.9	2.75	71.3	"
					Two solid solutions:
					(i) $K_2C_2O_4 \cdot H_2O$ in $(NH_4)_2C_2O_4 \cdot H_2O$ .
					(ii) $(NH_4)_2C_2O_4 \cdot H_2O$ in $K_2C_2O_4 \cdot H_2O$ .
14	1.216	26.3	1.83	71.9	Solid solution of $(NH_4)_2C_2O_4 \cdot H_2O$ in $K_2C_2O_4 \cdot H_2O$ .
15	1.216	26.8	0.85	72.3	"
16	1.215	27.2	—	72.8	$K_2C_2O_4 \cdot H_2O$ .



curves are obtainable at each of these temperatures, the two meeting sharply at a quadruple (or condensed triple) point.

There is no evidence at all of the existence of a double salt. On the other hand, it is quite apparent from the relations between compositions of solutions and corresponding residues (shown only for 50°) that the solid phase present in those complexes in which excess of ammonium oxalate is taken (curve *CB*) is not this pure solid, but contains in addition some potassium oxalate. The proportions of the two in the solid vary according to the composition of the solution in equilibrium, and the evidence is definite that mixed crystals of the two salts are produced. The more potassium oxalate there is in the solution, the more there is in the solid. The same must hold with regard to the solids in equilibrium along the curve *AB*. These solids will be mainly potassium oxalate with steadily increasing proportions of ammonium oxalate. The amounts of ammonium oxalate in solutions along this curve are, however, so small that a slight error in the analysis of the residue may make the extrapolation method uncertain in showing the solid phase.

Some of the mixed crystals were dried by draining on a porous tile in a closed vessel immersed in the thermostat. Analysis proved the two constituents of these mixed crystals to be the respective monohydrates.

The form of the isotherms, with a sharp change of direction at *B*, shows that two distinct solid phases must be present at this, a univariant, point. It follows that the series of mixed crystals is not complete, but that there is a limit to the solubility of each solid in the other. These limits have not been determined. The compositions are also not given by such points as *D* and *E* in Fig. 1, those of the exact solid solutions in equilibrium with the corresponding liquid solutions at the other ends of the tie-lines. Some of the crystals may have had a core of the pure main constituent, so that the mean composition represented by *D* and *E* may be low in potassium oxalate as compared with the solid solution itself. All that is established is the existence of mixed crystals.

The work of Foote and Andrew (*loc. cit.*) is not quite extended enough to show this. They obtained only the points *A*, *B*, and *C* at 25°.

It has been found impossible to repeat the work of Barbier (*loc. cit.*), which pointed to the formation of an anhydrous double salt,  $K_2C_2O_4 \cdot (NH_4)_2C_2O_4$ . By following closely the method which he described for isolating the compound, crystals were precipitated which, after drying on a porous tile, contained 81.1 per cent. of

ammonium oxalate, 5.8 per cent. of potassium oxalate, and (by difference) 13.1 per cent. of water. After washing with a solution of ammonia, as recommended by Barbier, the proportion of potassium oxalate decreased slightly. It appears certain that this precipitate consists of mixed crystals of the two hydrates.

It is of interest to note that Souchay and Lenssen (*loc. cit.*), following Wenzel's instructions for preparing the alleged double salt, obtained crystals which they stated to be ammonium oxalate, but containing 0.9 per cent. potash.

## II. System: $\text{Na}_2\text{C}_2\text{O}_4-(\text{NH}_4)_2\text{C}_2\text{O}_4-\text{H}_2\text{O}$ at $25^\circ$ and $50^\circ$ .

Sodium oxalate differs from both the potassium and ammonium salts in crystallising anhydrous from aqueous solution; hence it is less likely that mixed crystals will be formed between it and either of the other two. The figures in tables III and IV show that neither double salt nor mixed crystals occur in the sodium-ammonium system at  $25^\circ$  or  $50^\circ$ . The method of analysis was similar to that adopted for the previous system.

TABLE III.

25°.

Percentage composition of solution  
or residue (R).

No.	Density.	$\text{Na}_2\text{C}_2\text{O}_4$ .	$(\text{NH}_4)_2\text{C}_2\text{O}_4$ .	$\text{H}_2\text{O}$ .	Solid phases.
1	1.027	3.73	—	96.3	$\text{Na}_2\text{C}_2\text{O}_4$ .
2	1.030	3.69	0.74	95.6	
3	1.033	3.65	1.49	94.6	"
R 3	—	63.9	0.53	35.6	"
4	1.037	3.50	2.48	94.0	"
5	1.039	3.51	2.89	93.6	"
6	1.043	3.46	3.77	92.8	"
7	1.047	3.41	4.74	91.8	$\text{Na}_2\text{C}_2\text{O}_4$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ .
8	1.043	2.85	4.75	92.4	$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ .
9	1.035	1.82	4.81	93.4	"
R 9	—	0.40	66.9	32.7	"
10	1.028	0.89	4.88	94.2	"
11	1.021	—	5.01	95.0	"

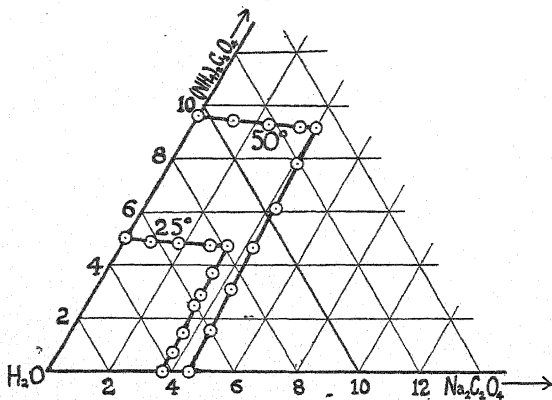
TABLE IV.

50°.

Percentage composition of solution  
or residue (R).

No.	Density.	$\text{Na}_2\text{C}_2\text{O}_4$ .	$(\text{NH}_4)_2\text{C}_2\text{O}_4$ .	$\text{H}_2\text{O}$ .	Solid phases.
1	1.023	4.54	—	95.5	$\text{Na}_2\text{C}_2\text{O}_4$ .
2	1.031	4.46	1.59	94.0	"
3	1.036	4.37	3.14	92.5	"
4	1.044	4.28	4.64	91.1	"
R 4	—	70.0	1.47	28.5	"
5	1.049	4.29	6.12	89.6	"
6	1.056	4.13	7.86	88.0	"
R 6	—	56.7	3.54	39.8	"
7	1.063	4.05	9.19	86.8	$\text{Na}_2\text{C}_2\text{O}_4$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ .
8	1.059	3.57	9.21	87.2	$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ .
R 8	—	1.47	63.4	35.1	"
9	1.051	2.45	9.32	88.2	"
10	1.042	1.25	9.46	89.3	"
11	1.034	—	9.63	90.4	"

FIG. 2.



The results are plotted in Fig. 2, where, on account of the sparing solubilities of the two components, only a single angle of the triangle is shown. The residues are omitted.

### III. System: $\text{K}_2\text{C}_2\text{O}_4$ - $\text{Na}_2\text{C}_2\text{O}_4$ - $\text{H}_2\text{O}$ at 25°.

Footo and Andrew (*loc. cit.*) concluded that anhydrous sodium oxalate and the monohydrate of potassium oxalate can exist side

by side in equilibrium with a common saturated solution, and the figures in table V, plotted in Fig. 3, confirm this, showing that neither double salts nor mixed crystals are formed. Solutions and residues were analysed by determining total oxalate by titration and total anhydrous salts by weighing after evaporation and drying at  $125^\circ$ , at which temperature potassium oxalate monohydrate is readily dehydrated. As the amount of sodium oxalate present is always relatively small, this indirect method is less accurate than that employed in the previous two cases.

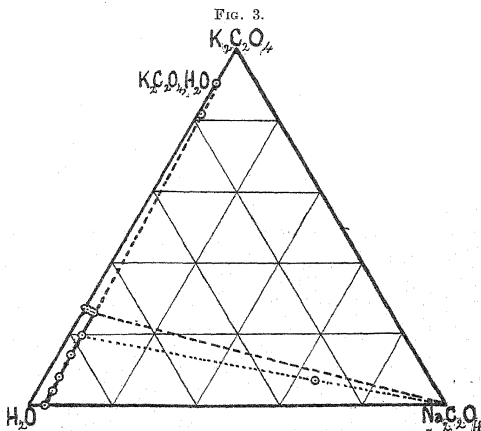


TABLE V.  
 $25^\circ$ .

Percentage composition of solution  
or residue (R).

No.	Density.	$K_2C_2O_4$ .	$Na_2C_2O_4$ .	$H_2O$ .	Solid phases.
1	1.215	27.2	—	72.8	$K_2C_2O_4 \cdot H_2O$ .
2	1.218	26.8	0.77	72.4	"
3	1.223	26.3	1.71	72.0	"
4	1.226	26.2	2.17	71.6	"
R 4	—	81.9	0.73	17.4	"
5	1.228	26.1	2.50	71.4	$K_2C_2O_4 \cdot H_2O$ and $Na_2C_2O_4$ .
6	1.178	19.6	3.21	77.2	$Na_2C_2O_4$ .
R 6	—	7.00	65.3	27.7	"
7	1.135	14.4	3.21	82.4	"
8	1.084	8.10	3.40	88.5	"
9	1.057	3.99	3.71	92.3	"
10	1.026	—	3.71	96.3	"

*Summary.*

(1) It has been stated by some authors and denied by others that potassium and ammonium oxalates form a double salt. Isotherms have been obtained at 25° and 50°, and show that at these temperatures mixed crystals of the monohydrates are formed.

(2) Anhydrous sodium oxalate has been shown to exist in equilibrium with ammonium oxalate monohydrate and a common, saturated solution at 25° and 50°. Neither double salts nor mixed crystals are formed.

(3) The same has been shown to be the case at 25° with anhydrous sodium oxalate and potassium oxalate monohydrate.

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### CXXVI.—*The Decomposition of Carbamide in the Presence of Nitric Acid.*

By TUDOR WILLIAMS PRICE.

WHILE investigating the use of dilute nitric acid as a nitrating agent at elevated temperatures, it was found that nitration was entirely inhibited by the addition of carbamide, although all the acid was used up. This reaction was considered worthy of further investigation, the results of which are given in the present communication.

The action of concentrated nitric acid on carbamide nitrate in the solid state at the ordinary temperature has been studied by Franchimont (*Rec. trav. chim.*, 1884, **3**, 216), who found that a gas was given off slowly, consisting of equal parts of carbon dioxide and nitrous oxide. The volume of gas was such that it contained all the carbon of the carbamide as carbon dioxide, and half the nitrogen as nitrous oxide, the other half forming ammonium nitrate.

No account has been found in the literature of the action of dilute nitric acid on carbamide, although the action of hydrochloric acid and sulphuric acid has been studied by Fawsitt (*Zeitsch. physikal. Chem.*, 1902, **41**, 601) and of hydrochloric acid by Werner (*T.*, 1918, **113**, 84).

Fawsitt (*loc. cit.*) found the reaction between carbamide and dilute hydrochloric and sulphuric acids to be unimolecular, which

he explained by the assumption that the former is first transformed to a small extent into ammonium cyanate at a measurable rate, and, if the inverse change is neglected, according to a unimolecular reaction. The ammonium cyanate is thereupon decomposed into the ammonium salt of the acid used, and carbon dioxide at a much greater rate than that at which ammonium cyanate is formed, and thus the decomposition of carbamide in the presence of hot acids is almost identical with the rate at which it is transformed into ammonium cyanate.

Werner (*loc. cit.*), on the other hand, states that the above assumption is quite unnecessary, and that the velocity of the reaction is regulated by the rate of dissociation of carbamide (at 100°) into ammonia and cyanic acid, when both products of dissociation are removed practically as fast as they are generated.

Whichever scheme of the mechanism of the reaction is correct, the final products are the same, namely, carbon dioxide and the ammonium salt of the acid used. If the action of hot dilute nitric acid on carbamide is the same as that of hydrochloric acid, the reaction should be unimolecular, and the products should be carbon dioxide and ammonium nitrate.

Veley (*Proc. Roy. Soc.*, 1892, 52, 27) has shown that nitric acid decomposes slowly at high temperatures, forming nitrous acid, the weaker the acid the higher being the temperature required for decomposition; also, it is well known that carbamide decomposes nitrous acid very readily, forming carbon dioxide and nitrogen. Hence it is possible that the true explanation of the disappearance of nitric acid when heated with carbamide in solution is the alternate formation of nitrous acid from nitric acid, and decomposition of the nitrous acid by carbamide. In this case, nitrogen will be present in the evolved gas, as well as carbon dioxide.

There are thus three separate methods of decomposition of carbamide by nitric acid, the gaseous products in each case being different. An analysis of the gas produced will then be of extreme importance.

As will be seen in the experimental part, the reaction between carbamide and nitric acid is unimolecular, and the gas evolved consists entirely of carbon dioxide.

#### EXPERIMENTAL.

The carbamide used was ordinary commercially pure carbamide recrystallised four times from absolute alcohol. The nitric acid solutions were made from pure distilled nitric acid, and contained



only a trace of nitrous acid. A normal solution of carbamide is taken to be one containing half its molecular weight in grams in a litre of water; all the other solutions of carbamide were made up on this basis.

Ten c.c. of the mixed solutions of carbamide and nitric acid were placed in hard-glass test-tubes, which were then sealed and placed in water at the required temperature. After various periods of heating, the tubes were withdrawn, cooled, opened, and their contents titrated with standard sodium hydroxide solution, using methyl-orange as indicator.

The majority of the experiments were made at 100°, but the reaction between *N*/2-carbamide and *N*/2-nitric acid was studied at 70°, 80°, 90°, and 100°.

The influence of certain salts on the velocity of the reaction was also examined.

In order to obtain figures comparable with those of Fawsitt, the velocity-constants for a unimolecular reaction were calculated according to the equation

$$k = \frac{1}{t_2 - t_1} \log_{10} \frac{a - x_1}{a - x_2},$$

instead of the correct equation,

$$k = \frac{1}{t_2 - t_1} \log_e \frac{a - x_1}{a - x_2},$$

where *a* is the initial concentration of carbamide, *x*<sub>1</sub> the amount of carbamide decomposed in time *t*<sub>1</sub>, and *x*<sub>2</sub> the amount decomposed in time *t*<sub>2</sub>. In every case, *t*<sub>1</sub> was fixed at sixty minutes, so as to obviate the error due to the time taken for the tube to reach the desired temperature.

*a*, *x*<sub>1</sub>, and *x*<sub>2</sub> were obtained from the titre of sodium hydroxide immediately after mixing the two solutions, and the titre after times *t*<sub>1</sub> and *t*<sub>2</sub>.

In one case, the constants for a bimolecular and termolecular reaction were calculated. \*

*Results.*—The results of two experiments are given in detail, and all are summarised in table I. It will be noted that the velocity-constant tends to increase towards the end of an experiment, and this is much more marked with *N*- and 2*N*-solution than with the more dilute ones.

Experiment 3. N-Carbamide + N-Nitric Acid at 100°.  $a = 50.40$ .

Time in minutes.	$a - x$ .	$k_1 \times 10^5$ (unimolecular).	$k_2 \times 10^6$ (bimolecular).	$k_3 \times 10^7$ (termolecular).
60	45.50	—	—	—
120	40.51	84	45	84
180	35.66	84	50	101
270	29.53	89	56	127
360	24.21	91	64	163
480	17.84	(97)	—	—
600	13.35	(98)	—	—
960	5.18	(105)	—	—
1500	1.21	(109)	—	—

Mean value  $k \times 10^5 = 87$ .

Experiment 5. N/2-Carbamide + N/2-Nitric Acid at 100°.  $a = 25.43$ .

Time in minutes.	$a - x$ .	$k \times 10^5$ .
60	22.75	—
120	19.81	101
180	17.25	100
270	13.96	101
360	11.39	100
480	8.29	105
600	6.36	102
900	3.00	104
1200	1.42	107
1500	0.83	(169)

Mean value  $k \times 10^5 = 102$ .

TABLE I.

Showing Velocity-constants obtained in the Decomposition of Carbamide.

Concentration of reaction mixture.	Temperature.	Duration of expt. in minutes.	No. of observations.	Mean value of $k \times 10^5$ .	Maximum variation of $k$ from mean.
2N-Carbamide + 2N-HNO <sub>3</sub> ...	100°	420	7	73	2.0
2N- " + N-HNO <sub>3</sub> ...	100	270	6	105	4.0
N- " + N-HNO <sub>3</sub> ...	100	360	5	87	4.0
N/2- " + N-HNO <sub>3</sub> ...	100	1800	9	88	3.0
N/2- " + N/2-HNO <sub>3</sub> ...	100	1200	9	102	5.0
N/4- " + N/2-HNO <sub>3</sub> ...	100	600	5	108	2.0
N/4- " + N/4-HNO <sub>3</sub> ...	100	420	7	111	3.0
N/8- " + N/8-HNO <sub>3</sub> ...	100	420	6	116	6.0
N/16- " + N/16-HNO <sub>3</sub> ...	100	360	7	133	8.0
N/2- " + N/2-HNO <sub>3</sub> ...	100	1500	10	122	5.0
N/2- " + N/2-NH <sub>4</sub> NO <sub>3</sub> ...	100	900	9	118	6.0
N/2- " + N/2-HNO <sub>3</sub> ...	100	420	5	118	3.0
N/2- " + N/2-NH <sub>4</sub> Cl ...	100	600	8	116	3.0
N/2- " + N/2-KCl ...	89	1800	9	23.0	2.8
N/2- " + N/2-HNO <sub>3</sub> ...	80	2790	9	9.3	0.7
N/2- " + N/2-HNO <sub>3</sub> ...	70	9360	10	2.4	0.3

*Experiment 17.*—Twenty-five c.c. of *N*-carbamide and 25 c.c. of *N*-nitric acid were heated at 100° in a boiling tube fitted with a reflux condenser. A delivery tube connected the top of the condenser to a nitrometer. The total air space from the level of the liquid in the boiling tube to the nitrometer was 34 c.c. One hundred c.c. of gas were collected in the nitrometer and rejected. It was considered that by this time all the air had been swept out of the apparatus, and collection of the gas for analysis was commenced. Fifty c.c. of this gas were almost entirely absorbed by a piece of moist potassium hydroxide, only a minute bubble being left. The gas was thus composed entirely of carbon dioxide, and did not contain any nitrous oxide or nitrogen, the small residue being either air which had not been completely swept out of the apparatus, or nitrogen from the trace of nitrous acid present in the nitric acid.

The heating of the carbamide and nitric acid solution was continued for fifty hours, at the end of which the solution was evaporated to dryness. On analysis, the residue was found to consist of ammonium nitrate with a little unchanged carbamide.

#### *Discussion of Results.*

The results show that the reaction between carbamide and nitric acid in dilute solution is undoubtedly unimolecular. The products consist entirely of carbon dioxide and ammonium nitrate. Hence the reaction is analogous to the decomposition of carbamide by hydrochloric or sulphuric acid, and is not due to the preliminary decomposition of nitric acid into nitrous acid with subsequent decomposition of the latter by carbamide.

On comparing the results with those obtained by Fawsitt for hydrochloric acid in table II, it will be seen that at all dilutions the velocity of reaction is greater with nitric acid than with hydrochloric acid.

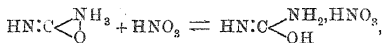
TABLE II.

*Showing Comparison between Velocity of Reaction at 100° of Carbamide with Nitric Acid and Hydrochloric Acid.*

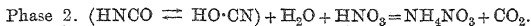
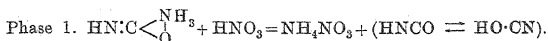
				$k \times 10^5$ .	
Reaction mixture.				HNO <sub>3</sub> .	HCl.*
2N-Carbamide	+ 2N-acid	.....		73	—
N-	+ N-	.....		87	58
N/2-	+ N/2-	.....		107	77
N/4-	+ N/4-	.....		111	90
N/8-	+ N/8-	.....		116	101
N/16-	+ N/16-	.....		133	101

\* Fawsitt's results.

The velocity of reaction diminishes regularly with an increase in the concentration of the nitric acid, and no maximum point was found such as Fawsitt found for hydrochloric acid (*loc. cit.*, p. 612). Fawsitt and Werner both state that only free carbamide is active. According to Werner, the equilibrium between carbamide and its nitrate can be represented as follows:



and the reaction between carbamide and nitric acid, on the analogy of the reaction between carbamide and hydrochloric acid, can be represented thus:



The diminution of the velocity with increase in concentration of the acid can thus be explained, since it is only "free" carbamide, and not carbamide "fixed" as its nitrate, which takes part in Phase 1 of the reaction.

Fawsitt found that the decomposition of carbamide in the presence of hydrochloric acid was retarded slightly by the addition of ammonium chloride, but was accelerated in the presence of sulphuric acid by the addition of ammonium sulphate. He also found that the decomposition of carbamide in the presence of water alone was accelerated by the addition of ammonium carbonate, sodium chloride, and potassium chloride, whilst ammonium chloride and ammonium hydrochloride had a decided retarding effect.

In the presence of nitric acid, the present author has found that ammonium nitrate, potassium nitrate, ammonium chloride, and potassium chloride all have a distinct accelerating effect on the decomposition of carbamide at *N*/2-concentration.

According to the dissociation theory of the decomposition of carbamide, the first action of heat on it is the production of ammonia and cyanic acid; in the presence of acids, this is followed by combination of ammonia with acid, forming an ammonium salt, and by hydrolysis of cyanic acid, forming an ammonium salt and carbon dioxide. The addition of the ammonium salt, or of any salt containing an ion common with the ammonium salt, to the reaction mixture, should therefore have a retarding effect on the velocity of decomposition. As shown by the experiments, this is not the case when carbamide is decomposed in the presence of nitric acid, and hence it would seem that the dissociation theory of

the decomposition of carbamide is not applicable in the presence of nitric acid.

The great influence of temperature on the velocity will be seen from table III.

TABLE III.

*Showing Effect of Temperature on Velocity of Reaction between N/2-Carbamide and N/2-Nitric Acid.*

Temperature.	$k \times 10^6$ .
100°	102.0
89	23.0
80	9.3
70	2.4

Below 80°, the velocity of decomposition of carbamide is small, and at 30° to 40° would be negligible; hence the use of excess of carbamide for the removal of nitrous acid from a mixture of nitrous acid and nitric acid will not be accompanied by loss of nitric acid as such if the temperature is not allowed to rise above 40°.

In conclusion, the author's best thanks are due to Messrs. Nobel's Explosives Company, Limited, and to Mr. William Rintoul, Manager of the Research Section, for the facilities afforded for carrying out this work and for permission to publish the results.

THE RESEARCH LABORATORIES,  
ARDEER.

[Received, November 6th, 1919.]

### CXXVII.—*Studies in Catalysis. Part XII. Catalytic Criteria and the Radiation Hypothesis.*

By WILLIAM CUDMORE McCULLAGH LEWIS.

THE criteria which have been suggested from time to time as applying to the phenomenon of catalysis are as follows (compare Rideal and Taylor, "Catalysis in Theory and Practice," Chap. 2):

(1) The chemical composition of the catalytic agents is unchanged on completion of the reaction process.

(2) Minimal amounts of a catalytic agent are adequate for the transformation of large quantities of the reacting substances.

(3) A catalyst does not affect the final state of equilibrium.

(4) A catalyst modifies the velocity of two inverse reactions to the same degree.

(5) A catalytic agent is incapable of starting a reaction; it can only modify the velocity of the reaction.

Criteria (1) and (2) are closely related, (2), in fact, being the corollary of (1). Both would be accepted at once provided secondary effects are excluded. To this extent they state a fact of experience, and indicate that catalysis is simply a special case of ordinary chemical reactivity.

Criteria (3) to (5), which form a group by themselves, are in a different category, as representing generalisations which may or may not be true. Criterion (4) is the corollary of (3), so that the group contains two distinct criteria. Considerable difference of opinion exists at the present time regarding the validity of these conclusions, according to the point of view adopted as the basis of criticism. It is of some interest, therefore, to examine criterion (3) or (4) and criterion (5) from the point of view of the radiation hypothesis of chemical reactivity.

We shall consider criterion (5) in the first place. On the radiation hypothesis, the possibility of a reaction occurring depends on the existence of radiation of a type or frequency absorbable by the reacting substance, the quantum of which radiation is sufficiently large to communicate the necessary critical increment to the molecule. In the case of thermal radiation, which is the kind of radiation envisaged in the quantum theory, theoretically all possible wave-lengths or frequencies are represented at any temperature. Consequently, the type of radiation necessary for any reaction is present in the space occupied by the matter, and therefore every reaction is correspondingly possible. This must include the so-called catalytic reactions as well as those to which this name is not applied. From this point of view, therefore, can we conclude that a catalyst does not initiate, but simply accelerates, a process which would occur, although under certain conditions infinitely slowly? This cannot be affirmed without qualification.

In the form in which criterion (5) is stated, it is evidently assumed that the same process *may* occur whether the catalyst be present or not, but this assumption is not necessarily true. It seems necessary to ascribe in certain cases, if not in all, a definite stoichiometric molecular mechanism to a catalyst, just as one would to any other reactant, and consequently, by adding such a catalyst, a new process commences (the origin of which is the field of radiation) that happens to give rise to certain end-products, which, we believe, might be attained in the absence of the catalyst. The fact appears to be that criterion (5), as ordinarily stated, involves a false antithesis. From the point of view of the radia-

tion hypothesis, a catalyst may be said either to render a reaction possible by supplying the necessary matter, or it may merely accelerate, according to circumstances. In no case is it the fundamental initiator of a process. The rôle played by the catalyst may be conveniently illustrated by the catalytic effect of an acid in the inversion of sucrose or the hydrolysis of an ester. Prior to the addition of the acid, the reaction is possible, involving reaction between a molecule of sucrose or ester and either a molecule of water or its ions, probably the undissociated molecule. On addition of the catalysing acid, the hydrogen ion accelerates the process already begun by the hydrogen ions already present. The undissociated molecule of the acid may also accelerate the reaction, but in doing so it is almost certain that it produces an intermediate substance, which was not formed in its absence. In so far as the intermediate stage is concerned, the molecule of the acid has rendered a new intermediate process possible, although the final products are independent of the nature of this intermediate stage. The real source or origin of initiation of any reaction, on the radiation hypothesis, is the radiation itself. The material catalyst, if it acts simply as a transformer, hastens a reaction which radiation has already initiated. The catalyst may also act as a molecular reactant, giving rise, under the stimulus of radiation, to new intermediate products. The validity of conclusion (5) depends, therefore, on the particular view adopted regarding the mechanism of the process. It seems that two distinct modes of mechanism are possible, and are apparently realised in the well-known acid catalyses. On one mode, the catalyst simply accelerates; on the other, it renders a new mechanism possible from the material point of view.

Turning now to criterion (3) or (4), which possesses much greater practical significance, the radiation hypothesis leads to the conclusion that, as a general principle, criterion (3) or (4) is certainly not true.

Let us take the simplest possible case of reversible reaction, represented by



The substance  $A$  is characterised by being capable of absorbing radiation of frequency  $\nu_A$ , as a result of which it is transformed into  $B$ . The substance  $B$  is likewise capable of absorbing radiation of frequency  $\nu_B$ , as a result of which the process is reversed. The heat evolved,  $Q$ , on passing from  $A$  to  $B$ , is then given by the expression

$$Q = Nh(\nu_B - \nu_A),$$

where  $N$  is the Avogadro number and  $Q$  is referred to one gram-molecule of  $A$  transformed.

Let us consider the special case in which  $v_A = v_B$ , or approximately so. In this case,  $Q$  is zero, or approximately so. A catalyst acting as a transformer will in this case be unable to distinguish between the two types of molecules  $A$  and  $B$ , since each is capable of absorbing the same type, or approximately the same type of radiation. It will therefore catalyze both the direct and the reverse reaction equally. That is, the opposing velocity constants will be equally increased, and the equilibrium constant will remain unaffected by the presence of the catalyst. This result is in harmony with the criterion.

If, on the other hand, the heat of the process is considerable, that is,  $v_A$  differs considerably from  $v_B$ , then it no longer follows that a positive catalyst will equally accelerate both reactions. In general, it would not be expected to do so, and consequently, in general, the equilibrium point will be affected by the catalyst. It is a significant fact, in view of the conclusion just drawn, that those reactions, such as esterification or hydrolysis, in which the equilibrium point is not sensibly affected by the catalyst, are precisely those in which the heat effect is small.

In the above case we have been considering mainly homogeneous catalysis by means of ions. Let us now take the case of catalysis by the undissociated molecule, such as the molecule of hydrochloric acid, which is generally regarded as functioning through the formation of an intermediate ternary compound. Thus, Falk and Nelson (*J. Amer. Chem. Soc.*, 1915, **37**, 1732) represent the intermediate oxonium complex in the case of hydrolysis of esters as (ester, HCl, H<sub>2</sub>O). In the reverse process, the corresponding compound is (carboxylic acid, HCl, alcohol). These two compounds are tautomeric, and may be identical. If they are identical, as Falk and Nelson assume, then the hydrochloric acid molecule will equally affect the direct and the reverse process, and thus leave the equilibrium point unchanged. This explanation of the mechanism of the effect produced by the undissociated molecule of the catalyzing acid has certainly the advantage of simplicity. It has this implication, however. Such additive compounds are generally formed rapidly compared with the rate of any further decomposition which they may undergo. If this is so, and if the same intermediate compound is formed in the hydrolysis as in the esterification, it would follow that the velocity constants should be the same, and the equilibrium constant should therefore be unity. This is not in agreement with experiment, although it is significant that the value of  $K$  is not greatly removed from unity. Thus, experiment has shown that

$$K = \frac{[\text{methyl acetate}] \times [\text{water}]}{[\text{methyl alcohol}] \times [\text{acetic acid}]} = 4.6$$



(compare Part V of this series of papers, T., 1916, 109, 71).

This ratio means that the velocity constant of esterification is 4.6 times the velocity constant of hydrolysis. On the radiation view, this ratio is mainly determined by the relative value of the exponential terms, that is, by

$$e^{-Nh\nu_1/RT} / e^{-Nh\nu_2/RT},$$

where  $Nh\nu_1$  is the critical increment of esterification and  $Nh\nu_2$  is the critical increment of hydrolysis, that is,

$$e^{Nh(\nu_2 - \nu_1)/RT} = 4.6.$$

At 300° absolute we find, therefore, that  $\nu_2 - \nu_1 = 1 \times 10^{13}$ . Both  $\nu_1$  and  $\nu_2$  do not, however, lie very far from the value  $2 \times 10^{14}$ , so that the difference in respect of position of absorption of infra-red radiation is extremely small, being of the order of one-twentieth of the absolute value of either frequency. The same idea is conveyed by saying that the heat effect does not exceed 1000 calories. The fact, therefore, that the equilibrium constant possesses a value not unity, but not far removed therefrom, means on the radiation basis that the intermediate compounds are not identical, but tautomeric, and, further, that both kinds of molecule absorb almost the same frequency, so that any change in the equilibrium constant introduced by altering the concentration of the catalyst is insensible. (It may be noted that the relatively large change in  $K$  observed by Lapworth has its origin, as Lapworth has shown, in what is virtually a distinct reaction not directly connected with the actual esterification-hydrolysis process itself.) In the case considered we conclude, therefore, that as a practical guide the criterion (3) or (4) is true, that is, in those cases in which the equilibrium constant is not far removed from unity. The conclusion is obviously comparable with that drawn in connexion with ion catalysis.

In addition to homogeneous catalysis by dissolved substances in a given solvent, it is well known that different solvents themselves exert their own catalytic effect. From the point of view of radiation, we conclude that in this type of catalysis criterion (3) or (4) cannot, in general, be even approximately true, since each solvent is characterised by its own electromagnetic properties, that is, by its power of absorption at different wave-lengths, which differs from solvent to solvent, and consequently entails a different distribution of radiation density. The particular type of radiation required by the reactant is therefore present to a different extent, according to the nature of the solvent, and consequently the

velocity constant and equilibrium constant is a function of the solvent. Specific differences are further introduced by the mutual interaction of solvent and solute, whereby the effective frequency itself is altered to a slight extent.

Finally, as regards heterogeneous catalysis, evidence has been collected and presented by Bancroft (*J. Physical Chem.*, 1917, **21**, 573; 1918, **22**, 433) to show that the catalyst affects the equilibrium point of the process. Heterogeneous catalysis has been examined in a preliminary manner from the point of view of radiation (T., 1919, **115**, 182), and it is concluded that the equilibrium point must be a function of the nature and extent of the catalytic material, owing to the alteration in the values of the critical increments which is introduced by the presence of the catalyst. The catalytic layer here considered is only one molecule, or possibly two molecules, in thickness, that is, it is of the order  $10^{-8}$  cm. In this layer, the final amounts of reactants and resultants will differ, in general, from the true equilibrium amounts characteristic of the homogeneous gas phase, for in the adsorption layer the relative amounts are determined by the relative adsorption capacities. If this is a complete statement of the phenomenon, it is evident that criterion (3) or (4) is inapplicable. There is, however, a further possibility to be considered.

The adsorbed reactants and resultants are in an activated condition as long as they are actually in the adsorption layer. In time, they necessarily pass out into the homogeneous gas phase, owing to desorption. If these molecules at the moment of leaving the adsorption layer lose the extra energy which they possess and become immediately transformed into molecules of normal energy content, it follows that their relative concentration in the homogeneous gas phase becomes identical with that in the adsorption layer, for, in general, the reaction in the homogeneous phase is extremely slow. There is the possibility, however, that the activated reactants and resultants on leaving the true adsorption layer do not immediately revert to the inactive state, but may retain their activity for a short space corresponding, perhaps, with a layer  $10^{-6}$  cm. in thickness. If this is the case, there will be a rapid chemical change in this *extra*-adsorption layer, which will tend to bring the concentrations of the reactants and resultants into the ratio required by the law of mass action for the homogeneous phase. Whether the true equilibrium point would be attained or not would depend on the average life of the activated molecules. At moderately high temperatures, the average molecular velocity may be taken to be  $10^5$  cm. per second; hence it would require  $10^{-11}$  second for a molecule to traverse a distance

of  $10^{-6}$  cm. It is possible that the activated state may be maintained for a longer period of time than this, and therefore the more likely is the process to attain the true equilibrium position. The more selective the nature of the adsorption material, the further, in general, will the "equilibrium" of the adsorption layer depart from the true mass action equilibrium. Hence, even if such a compensating effect as that suggested above actually operates, criterion (3) or (4) cannot be regarded as valid.

It is concluded, therefore, that criterion (3) or (4) is, in general, not true; in homogeneous systems it approximates more closely to experiment the smaller the heat effect accompanying the reaction; in heterogeneous systems it is not certain whether even this approximation to validity holds good.

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[Received, October 31st, 1919.]

### CXXVIII.—*Criteria of the Degree of Purity of Commercial Toluene.*

By JOHN SCOTT LUMSDEN.

THE following investigation was undertaken for the Explosives Department of the Ministry of Munitions for the purpose of finding some easily applied method for estimating the degree of purity of commercial toluene, and is published with the permission of the Department.

Commercial toluene contains varying amounts of a liquid which cannot be nitrated and has distilled along with the toluene during rectification. This liquid has not been isolated, but in the following tests the assumption is made that it may be represented by a paraffin mixture which boils close to the boiling point of toluene. By fractionation of petrol, a quantity of such a liquid was obtained boiling at  $108-112^{\circ}$ .

*Estimation of Toluene by Specific Gravity.*—Pure toluene at  $15^{\circ}$  was found to have  $D\ 0.8712$ ; the paraffin mixture had  $D\ 0.743$ . Since there is no change in volume on mixing toluene and paraffin, a graph was prepared to show the density of mixtures. From this graph, it was found that the presence of 1 per cent. of paraffin produced a lowering of the density of  $0.0013$ .

Whilst such a graph may not be depended on to give the accurate

percentage of impurity present, because the toluene may be moist and the impurity may not be like that assumed, it is certainly useful in indicating poor samples. For example, of two samples of commercial toluene, (a) had D 0.872 and (b) 0.8613. Both were fractionated, with the following results: Sample (a) showed a trace of moisture, then boiled steadily at  $110^{\circ}$ . All fractions, right to the end, had D 0.8716. This was therefore a very good sample of toluene. Sample (b) showed a little moisture, and then boiled half a degree below, slowly rising to half a degree above  $110^{\circ}$ . The fractions had D 0.8623, 0.8621, 0.8622, 0.8619, 0.8612, 0.8586, and 0.8570. The original low density and the decreasing density of the fractions pointed to a considerable admixture of paraffins; from the graph, the indication is 7.7 per cent.

*Estimation of Toluene by Nitration.*—To effect nitration, potassium nitrate and sulphuric acid were employed, as described later. It was soon found that the nitration of toluene cannot be made to stop when the mononitro-compound is formed, but that any excess of acid is used up, producing the dinitro-compound; it was, however, proved, as the result of many experiments, that nitration stops quantitatively when all the toluene has been converted into the dinitro-compound.

Using nitration as a means of estimating toluene, there are obviously two methods which may be adopted, namely, by nitrating with a weighed excess of potassium nitrate, and determining the weight of nitric acid remaining after nitration, the amount of acid used is obtained, and from that the weight of toluene nitrated, or by isolating and weighing the dinitro-compound. Adopting the first method, it was found that the residual acid could be satisfactorily determined by the nitrometer, but that by the second method the dinitro-compound could not be completely recovered, because a small but definite amount remains in solution in the acid liquid from which the substance is filtered.

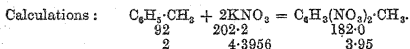
The nitration process is as follows. A 100 c.c. flask is weighed, and into this is weighed accurately, by dropping from a fine pipette, 2 grams of the sample to be nitrated. Five grams of pure dry powdered potassium nitrate are weighed in a watch-glass or aluminium scoop, and transferred with great care to the flask. The flask is cooled in water, and 30 c.c. of pure concentrated sulphuric acid are poured in rapidly, the flask being shaken continuously to prevent the formation of solid lumps, which, if formed, take some time to dissolve. When the action is over, a pale yellow, homogeneous liquid is obtained.

To cause the dinitro-compound to separate, about 60 c.c. of water are added, the first few c.c. being dropped in slowly, lest

the heat evolved should volatilise any nitric acid, and at the same time the flask is cooled in water.

The solid is obtained in soft flakes which are nearly white, and when the contents of the flask are quite cold, the separation may be considered complete. Filtration is effected by the aid of the pump, using a small porcelain funnel with a small filter paper; the preparation flask is washed out with several small amounts of water, which are poured through the funnel, and the solid is washed free of acid. The filtrate is transferred to a graduated cylinder, and, together with the washings of the filter flask, is made up to exactly 150 c.c.

The whole operation of nitration proceeds smoothly, and the only point where care is needed is when adding water to the nitrated liquid, great precautions being then necessary to avoid rise of temperature.



(a) Two grams of toluene require for nitration 4·39 grams of potassium nitrate. One per cent. of this—0·0439 gram—remaining unused, represents 1 per cent. of impurity in the toluene. 0·004522 Gram of potassium nitrate gives 1 c.c. of gas in the nitrometer; 0·0439 gram therefore represents 9·72 c.c. Working with 2 grams of toluene, 9·72 c.c. of gas in the nitrometer at *N.T.P.* represent 1 per cent. of impurity.

(b) Five grams of potassium nitrate are used to nitrate 2 grams of toluene, but only 4·3956 grams are required. This is an excess of 0·6044 gram, which in the nitrometer would give 133·65 c.c. of gas.

(c) Two grams of toluene give 3·95 grams of dinitrotoluene. One per cent. of this—0·0395 gram—as a deficit in the yield, represents 1 per cent. of impurity in the toluene.

*Examples of Nitration.* (a) *Estimation by Nitrometer.*—Two grams of toluene were nitrated with 5 grams of potassium nitrate. The liquid was made up to 150 c.c., and 15 c.c. were taken for the nitrometer estimation. (The 15 c.c. were measured from a small burette into the cup of the nitrometer, and 10 c.c. of pure sulphuric acid were used to liberate the gas.) 19·8 C.c. of gas at 16° were obtained, or 18·71 at *N.T.P.* For the whole 150 c.c. this was 187·1 c.c.; deducting the known excess used, namely, 133·65 c.c., leaves 53·45 c.c. As 9·72 c.c. represent 1 per cent. of impurity, 53·45 c.c. represent 5·5 per cent. of impurity.

The following are the results of other estimations:

Pure toluene.	Good toluene.	Poor toluene.
150 c.c. liquid, 15 c.c. taken.	175 c.c. liquid, 20 c.c. taken.	150 c.c. liquid, 15 c.c. taken.
13.27 c.c. gas at N.T.P.	15.7 c.c. gas at N.T.P.	18.64 c.c. gas at N.T.P.
For 150 c.c. liquid, 132.7 c.c.	For 175 c.c. liquid, 137.37 c.c.	For 150 c.c. liquid, 186.4 c.c.
From excess taken 133.6	From excess 133.65	From excess 133.6
— 0.9 c.c.	3.72 c.c.	52.8 c.c.
— $0.9/9.72 = 0.1$ per cent.	$3.72/9.72 = 0.38$ per cent.	$52.8/9.72 = 5.4$ per cent.
Toluene 100.1 per cent.	Toluene $100 - 0.38 = 99.62$ per cent.	Toluene $100 - 5.4 = 94.6$ per cent.

The sample of pure toluene shows more than 100 per cent.; this is due to experimental loss. It will be realised that if the potassium nitrate is not pure and dry, or if there is any loss before the filtrate is made up to a definite volume, less nitric acid is found, and this is indicated as a small increase in the percentage of toluene.

(b) *Estimation by Weighing the Solid.*—The solid dinitro-compound is transferred from the filter funnel to a watch-glass and set in a desiccator over sulphuric acid, or the watch-glass may be set over a beaker of boiling water, when the solid melts to a clear liquid with water beneath it. On cooling, the solid forms a firm mass, from which water is readily removed by filter paper; then, after a much shorter time in the desiccator, the weight becomes constant.

It was found that when the volume, after nitration, was made up to 150 c.c., approximately 0.11 gram of solid remained in solution, and this amount is added to the weight found in the following examples.

Two grams of "pure" toluene gave 3.8337 grams of solid; adding 0.11 gram, the total dinitro-compound was 3.9437 grams; 100 per cent. toluene should give 3.9564 grams, therefore the deficit is 0.0127 gram.  $0.0395$  Gram deficit represents 1 per cent. of impurity, and 0.0127 gram 0.32 per cent. The toluene was therefore  $100 - 0.32 = 99.68$  per cent.

Two grams of a poor sample of toluene gave a deficit of 0.2573 gram, that is,  $0.2573/0.0395 = 6.5$  per cent. The toluene was therefore  $100 - 6.5 = 93.5$  per cent.

#### *Estimation of Toluene by Miscibility with Acetic Acid.*

Whilst engaged on this investigation, a report by Professor Orton was received describing the experimental work detailed in his recent paper (this vol., p. 1055). He there showed that when

88 to 90 per cent. acetic acid is mixed with toluene in the proportions of 1 c.c. of acid to 0.8 c.c. of toluene, two layers are formed, and on raising the temperature, a point of complete miscibility is reached which is definite for the same strength of acid, and so sharply defined that it can be read to one-tenth of a degree. He showed also that the temperature of miscibility of toluene rises regularly with the dilution of the acetic acid, and further, that for a given strength of acid the temperature of miscibility of toluene containing paraffin rises in direct proportion to the amount of paraffin present.

Working with two strengths of acetic acid, 87.9 and 89.5 per cent., and using pipettes of certain volumes, he prepared curves from which the percentage of a mixture of toluene and paraffin could be found when the temperature of miscibility with one of these acids had been determined. The method is susceptible of great accuracy, but it is very troublesome to prepare acetic acid of a definite strength, and almost impossible to keep a concentrated acid without absorption of moisture from the air, and, moreover, it requires so much care to carry out the process as set down by Professor Orton that it could scarcely be used as a commercial test. The following modification, consisting in the changing of an absolute to a comparative method, may, however, be carried out in any commercial laboratory.

A quantity of concentrated acetic acid of unknown strength is taken, and with equal volumes of this, the temperatures of miscibility with equal volumes of pure toluene, toluene with 5 per cent. of paraffins, and the sample of toluene to be tested, are found. Then, since the percentage of paraffins is proportional to the increase in the temperature of miscibility, the comparison of the rise of temperature of miscibility of the sample with that of the 5 per cent. paraffin mixture gives the paraffin content of the sample.

To carry out the test, there is required:

- (1) A quantity of pure toluene, which need not be synthetically pure, but might be considered as 100 per cent. quality.
- (2) A mixture of this toluene with 5 per cent. of paraffins, made by mixing 95 grams of toluene with 5 grams of paraffins of the same boiling point, prepared by the distillation of petrol.
- (3) Acetic acid, prepared by taking 100 grams of glacial acetic acid, adding a few c.c. of water, and, by trial with toluene in the proportions described below, finding if two layers are formed and if the temperature of miscibility is somewhere between 25° and 30°.
- (4) The sample to be tested.

The proportions of acetic acid and toluene found by Professor

Orton as suitable for the test may be adhered to, and two pipettes prepared, one delivering 1 c.c. and the other 0.8 c.c., or quantities in these proportions, but they need not be exact. The pipettes are made from narrow glass tubing, and must have fine capillary points to deliver very slowly. A test-tube 1.2 cm. in diameter serves as a vessel in which the miscibility point is determined, and while the test is being made it may for convenience be fixed to the thermometer by a rubber band. The test is carried out as follows. With the larger pipette, acetic acid is run into the test-tube, and pure toluene is added from the smaller pipette. The tube is then fixed to the thermometer, which must be graduated in tenths of a degree. Water is heated in a beaker holding about 2 litres, the temperature being raised speedily, and by stirring with the thermometer and tube, an approximation to the miscibility point is found by noting the temperature when the two layers disappear and a homogeneous liquid is obtained.

A little cold water is then added to the beaker, the flame is turned very low, the water thoroughly stirred, and as the temperature slowly rises, the thermometer and tube are moved continuously in the water. As the miscibility point is approached, the two layers disappear, the liquid becomes opalescent, and then suddenly becomes transparent. This is the point at which the temperature is noted. By cooling the water in the beaker  $1^{\circ}$ , the test may be repeated.

The same procedure is gone through with the 95 per cent. toluene and with the sample being examined, the tube being washed out thoroughly each time and dried in an air-oven. The following are results obtained:

	Pure toluene.	95 Per cent. toluene.	Sample.
(1) The miscibility temperature was	$32.0^{\circ}$	$38.3^{\circ}$	$41.4^{\circ}$
(2) Same sample on another day, the acid being different .....	33.4	40.3	44.0

From (1)  $38.3^{\circ} - 32^{\circ} = 6.3^{\circ}$ , and  $41.4^{\circ} - 32^{\circ} = 9.4^{\circ}$ . A rise of  $6.3^{\circ}$  represents 5 per cent. of impurity,  $9.4^{\circ}$  represents 7.4 per cent.

From (2)  $40.3^{\circ} - 33.4^{\circ} = 6.9^{\circ}$ , and  $44.0^{\circ} - 33.4^{\circ} = 10.6^{\circ}$ . A rise of  $6.9^{\circ}$  represents 5 per cent. of impurity,  $10.6^{\circ}$  represents 7.6 per cent.

It is seen that the strength of the acid does not require to be known: it has only to remain constant during the time that three portions are withdrawn, and the pipettes do not require to be of any definite volume, although they must deliver precisely the same volume each time.

The three tests might be carried out simultaneously by having three test-tubes attached to the thermometer, one with each mixture,



and the three points of miscibility determined as the temperature of the water is raised.

When the same sample of toluene was tested by the different methods, the following results were obtained:

From specific gravity curve .....	92.3 per cent.
From nitrometer estimation after nitration .....	92.9 „
By weighing dinitro-compound .....	92.6 „
By temperature of miscibility with acetic acid .....	92.5 „

*Conclusions.*—The specific gravity of commercial toluene gives a fair indication of the amount of impurity present; the estimation of the temperature of miscibility with acetic acid is quickly done, and, although a comparative method, if skilfully carried out is trustworthy; the nitration and estimation of the excess of nitric acid by the nitrometer is believed to be the most accurate test and indicates the total nitration which has taken place, and the weighing of the solid after nitration gives the actual practical yield of nitro-compound.

By none of the methods, under ordinary conditions of working, can an accuracy closer than one-half per cent. be expected.

THE TECHNICAL COLLEGE,  
DUNDEE.

[Received, October 16th, 1919.]

## CXXIX.—1:3-Benzodiazolearsinic Acids and their Reduction Products.

By ROBERT REGINALD BAXTER and ROBERT GEORGE FARGHER.

SINCE the discovery of salvarsan (Ehrlich and Bertheim, *Ber.*, 1912, 45, 756), many attempts have been made to prepare derivatives or closely allied products which would render unnecessary the somewhat elaborate technique involved in the clinical use of the original compound, which, owing to its pronounced acidity, has to be converted into the disodium salt, in turn alkaline in reaction, before use. Neosalvarsan, the sodium *N*-methylenesulphinate of salvarsan, introduced to avoid these difficulties, possesses many advantages, such as ready solubility and neutral reaction, but, in spite of these, there is a consensus of opinion in favour of salvarsan, as its spirochaeticidal action appears to be stronger and more certain.

In this and in other cases the attempts have led to the formation of acid derivatives giving neutral salts with alkalis. The authors desired, on the other hand, to obtain hydrochlorides soluble in water and sufficiently less acid in reaction than salvarsan to admit

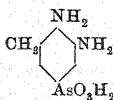
of their direct use, and it was with this object in view that the present investigation was commenced, since it was considered probable that the hydrochlorides of the arsenobenzenes derived from 1:3-benzodiazole (benzglyoxaline) would fulfil these requirements. Further, considering the properties of the glyoxaline nucleus, they might be expected to exert acidic as well as basic properties, and thus closely resemble salvarsan itself.

Additional interest would attach to such compounds in view of their relationship to 3:4:5:3':4':5'-hexa-aminoarsenobenzene and its *N*-methyl derivatives (D.R.-P. 286667, 286668, 286854, 286855, 294276; E.P. 7488 and 8041 of 1913; U.S.P. 1081079; Benda, *Ber.*, 1914, **47**, 1316; Karrer, *Ber.*, 1916, **49**, 1448), which are stated to possess the unexpected property of dissolving in alkali hydrogen carbonates, forming carbamates with the same degree of alkalinity as that of normal blood serum and a relatively low toxicity (D.R.-P. 269660; E.P. 1667 of 1914).

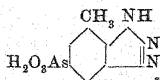
So far as the authors are aware, the benzodiazolearsinic acids have not been examined, Bertheim (*Ber.*, 1911, **44**, 3092), who described 3:4-diaminophenylarsinic acid and several of its derivatives, making no mention of them. They are, however, readily obtained by the well-known reaction of ortho-diamines with formic or acetic acid, whereby the acyl derivative first formed suffers loss of a molecule of water if a monoacyl, or of a molecule of acid if a diacyl derivative, with consequent closing of the ring (compare Ladenburg, *Ber.*, 1875, **8**, 677; Wundt, *Ber.*, 1878, **11**, 826).

The comparative stability of 3:4-diacetylaminophenylarsinic acid, which crystallises from boiling water unchanged, and does not alter save for slight decomposition when heated at 250°/20 mm., and, generally, the stability of diacyl-*o*-diamines (compare Bistrzycki and Ulfers, *Ber.*, 1890, **23**, 1876), seems to indicate that in the absence of anhydrides the reaction proceeds with intermediate formation of a monoacyl derivative.

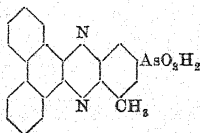
5:6-Diamino-*m*-tolylarsinic acid (I), which, together with 3:4-diaminophenylarsinic acid (Bertheim, *loc. cit.*), formed the starting material for the investigation, was obtained by the reduction of 5-nitro-6-amino-*m*-tolylarsinic acid (this vol., p. 989) with sodium hyposulphite. It undergoes all the condensations typical of an



(I.)



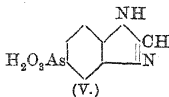
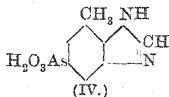
(II.)



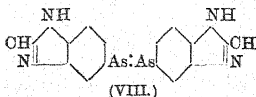
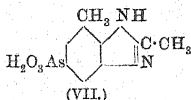
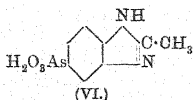
(III.)

o-diamine, giving, for example, with sodium nitrite in acid solution, 7-methyl-1:2:3-benzotriazole-5-arsinic acid (II), and with phenanthraquinone, 4-methylphenanthraphenazine-2-arsinic acid (III). The latter derivative shows the colour reactions characteristic of phenanthraphenazine.

With boiling glacial formic acid, the acids readily yielded 7-methyl-1:3-benzodiazole-5-arsinic acid (IV) and 1:3-benzodiazole-5-arsinic acid (V) respectively.



The action of acetic acid did not proceed quite so smoothly. 3:4-Diaminophenylarsinic acid, although stated (Bertheim, *loc. cit.*) to be readily soluble in acetic acid, is far from being so, and, on boiling with acetic acid, acetic anhydride, or a mixture of the two, gives rise to very highly coloured products, which are difficult to purify. If the reaction is carried out as described in the experimental portion of this paper, the main product is 3:4-diacetylaminophenylarsinic acid, which, on heating with water in a sealed tube at 130°, yields 2-methyl-1:3-benzodiazole-5-arsinic acid (VI). In the case of the higher homologue, the desired reaction takes place predominantly, with the formation of 2:7-dimethyl-1:3-benzodiazole-5-arsinic acid (VII). Incidentally, it may be mentioned that it has since been found that if 3:4-diaminophenylarsinic acid, dissolved in the requisite amount of sodium hydroxide (40 per cent. solution) to form the monosodium salt, is treated with sufficient acetic anhydride to neutralise the sodium hydroxide and form acetic acid with the water present, and then boiled, the main product of the reaction is the benzodiazole derivative.



The reduction of the above acids with hypophosphorous acid, although it proceeds normally, leads to gelatinous products difficult

to handle, and consequently the reduction was carried out by means of sodium hyposulphite. This gives pale yellow *arsenobenzenes*, insoluble in water, which were converted into hydrochlorides by precipitating their solutions in acetic acid with excess of hydrochloric acid, or by treating the suspensions of the bases in water with just sufficient hydrochloric acid to bring about solution, and precipitating as before. The *hydrochlorides* form pale yellow powders, soluble in water, but very sparingly so in the usual organic solvents. Their aqueous solutions react strongly acid to litmus, but neutral to methyl-orange.

It was expected that this acidity would prove too great for purposes of intravenous injection, and that it would be difficult to distinguish between the effect due to the acidity and that due to the arsenic compound. This was confirmed by experiments with 5:5'-*arseno-1:3:1':3'-benzodiazole* (VIII) by Miss Soref, of the Wellcome Physiological Research Laboratories.

#### EXPERIMENTAL.

##### 3:4-Diaminophenylarsinic Acid.

The preparation of considerable quantities of this acid was carried out according to the directions given by Bertheim (*loc. cit.*), save that it was found advisable to omit the boiling of the solution after the reduction with sodium hyposulphite, as this diminished the yield and gave a more highly coloured product.

##### 1:3-Benzodiazole-5-arsinic Acid (V).

Ten grams of 3:4-diaminophenylarsinic acid were boiled under a reflux condenser for six hours with 100 c.c. of glacial formic acid. After removal of the excess of formic acid by distillation, water was added, when 7.5 grams of crystalline material rapidly separated. To remove adhering traces of colouring matter, the product was treated with charcoal in dilute alkaline solution. On making neutral to methyl-orange, crystallisation commenced at once, practically the whole being recovered in a pure state.

1:3-Benzodiazole-5-arsinic acid crystallises from water, in which it is sparingly soluble, in clusters of minute, flattened prisms, which are anhydrous. On heating, it gradually darkens above 250° and decomposes rapidly about 297° (corr.).

Found: N=11.4; As=30.8.

$C_7H_7O_3N_2As$  (242.1) requires N=11.6; As=30.96 per cent.

*5:5'-Arseno-1:3:1':3'-benzodiazole (VIII).*

A solution of 5 grams of 1:3-benzodiazole-5-arsinic acid in 100 c.c. of water containing 1.2 grams of sodium hydroxide was treated with 50 grams of sodium hyposulphite and 11.5 grams of magnesium chloride dissolved in 300 c.c. of water, and the mixture heated, with stirring, at 60° for two hours in an atmosphere of carbon dioxide, by which time the precipitation of the yellow arsenobenzene was complete. After cooling, the product was collected, well washed with water, suspended in 90 c.c. of water, dissolved by the addition of sufficient hydrochloric acid to form the dihydrochloride, filtered from traces of undissolved matter, and precipitated by pouring into an equal volume of concentrated hydrochloric acid. The hydrochloride was collected, well washed with alcohol and ether, and dried in a vacuum over sulphuric acid. The yield amounted to 3.9 grams.

*5:5'-Arseno-1:3:1':3'-benzodiazole* is obtained as a bright yellow powder practically insoluble in water or the usual organic solvents, sparingly, if at all, soluble in methyl alcohol containing hydrochloric acid, but fairly readily so in 50 per cent. acetic acid. The *dihydrochloride* forms a pale yellow powder soluble in water, very sparingly so in methyl alcohol or ethyl alcohol, and quite insoluble in acetone or ether. The aqueous solution reacts acid to litmus, but neutral to methyl-orange. After drying in a vacuum overnight, it retains solvent equivalent to two molecules of water.

Found: N=11.3; As=30.2; Cl=13.8.

$C_{14}H_{10}N_4As_2 \cdot 2HCl \cdot 2H_2O$  (493.1) requires N=11.4; As=30.4; Cl=14.4 per cent.

*3:4-Diacetylaminophenylarsinic Acid and 2-Methyl-1:3-benzodiazole-5-arsinic Acid (VI).*

Experiments in which diaminophenylarsinic acid was heated with glacial acetic acid, with acetic anhydride, with acetyl chloride and pyridine, or with acetic anhydride in the presence of a trace of sulphuric acid, were unsuccessful, owing to the considerable amount of decomposition which occurred. It was found, however, that if the acid, dissolved in methyl alcohol, was treated with a mixture of acetic acid and acetic anhydride, and the methyl alcohol then removed as completely as possible by distillation on the water-bath, the resulting solution, after heating to active boiling for four hours, gave an excellent yield of a product, which, from its composition, proved to be the diacetyl derivative of diaminophenylarsinic acid.

*3:4-Diacetylaminophenylarsinic acid* crystallises from water, in

which it is fairly readily soluble, as a felted mass of fine needles which retain from 2 to 2.5 per cent. of solvent.

Found: loss at  $110^{\circ}$  (two specimens) 2.6, 2.2.

In dried material: N=8.8; As=23.8.

$C_{10}H_{13}O_5N_2As$  (316.1) requires N=8.9; As=23.7 per cent.

As the product did not lose acetic acid when heated to  $250^{\circ}$ /20 mm., it was heated with ten times its weight of water in a sealed tube for four hours at  $130^{\circ}$ , when the desired reaction took place almost completely.

*2-Methyl-1:3-benzodiazole-5-arsinic acid* crystallises from water, in which it is somewhat sparingly soluble, in minute needles containing two and a-half molecules of water of crystallisation, the last half molecule being removed with difficulty at  $110^{\circ}$ , but fairly readily at  $120^{\circ}$ . After drying at  $110^{\circ}$ , it darkens on heating above  $250^{\circ}$  and decomposes at about  $270^{\circ}$  (corr.).

Found: loss at  $110^{\circ}$ =15.5.

$C_8H_9O_3N_2As \cdot 2\frac{1}{2}H_2O$  requires  $H_2O$ =15.0 per cent.

In dried material: C=37.3; H=3.8; N=10.7; As=29.3.

$C_8H_9O_3N_2As$  (256.1) requires C=37.5; H=3.5; N=10.9; As=29.3 per cent.

#### 2:2'-Dimethyl-5:5'-arseno-1:3:1':3'-benzodiazole.

This was prepared in the same manner as 5:5'-arseno-1:3:1':3'-benzodiazole, which it resembles very closely in its properties.

The *dihydrochloride* forms a pale yellow powder, soluble in water, but almost completely insoluble in methyl alcohol, ethyl alcohol, ether, or acetone. After drying in a vacuum for twenty-four hours, it retains solvent approximating to three molecules of water. In aqueous solution it reacts acid to litmus but neutral to methyl-orange.

Found: N=10.3; Cl=12.7; As=28.0.

$C_{16}H_{14}N_4As_2 \cdot 2HCl \cdot 3H_2O$  (539.1) requires N=10.4; Cl=13.1; As=27.8 per cent.

#### 5:6-Diamino-m-tolylarsinic Acid (I).

A solution of 8.6 grams of 5-nitro-6-amino-m-tolylarsinic acid in 75 c.c. of water and 6.2 c.c. of 10*N*-sodium hydroxide was cooled to  $-1^{\circ}$  and treated, in one operation, while stirring vigorously, with 20.4 grams of sodium hyposulphite. When the reaction was complete, as shown by the change in colour, the solution was filtered, treated with 8.1 c.c. of hydrochloric acid (D 1.12), and the resulting acid, which separated in the course of a few minutes,

collected, washed with water, and recrystallised from water, in which it is sparingly soluble in the cold, but fairly readily so on warming. It separates in colourless needles, which contain between one and a-half and two molecules of water of crystallisation. It dissolves fairly readily in methyl alcohol or acetic acid, but is very sparingly soluble in ether, benzene, or petroleum. Its solution in dilute hydrochloric acid gives a characteristic, deep violet coloration with a drop of a dilute solution of potassium dichromate. It appears to decompose slowly on keeping.

Loss at  $110^{\circ} = 11.2$ .

$C_7H_{11}O_3N_2As, 1\frac{1}{2}H_2O$  requires 9.9 per cent.

$C_7H_{11}O_3N_2As, 2H_2O$  requires 12.8 per cent.

In dried material: N=11.3; As=30.4.

$C_7H_{11}O_3N_2As$  (246.1) requires N=11.4; As=30.5 per cent.

*7-Methyl-1:2:3-benzotriazole-5-arsinic acid* (II) was obtained by treating a solution of 3:4-diamino-*m*-tolylarsinic acid in dilute hydrochloric acid with a molecular proportion of sodium nitrite. It forms a crystalline powder very sparingly soluble in water, but more readily so in alcohol. It crystallises from 50 per cent. alcohol in minute, colourless, glistening needles, which are anhydrous, and gradually decompose on heating above  $280^{\circ}$ .

Found: N=16.6.

$C_7H_8O_3N_3As$  (257.1) requires N=16.4 per cent.

*4-Methylphenanthraquinazoline-2-arsinic acid* (III) was obtained by the condensation of molecular proportions of phenanthraquinone and 3:4-diamino-*m*-tolylarsinic acid in acetic acid solution. It forms an amorphous, yellow powder, sparingly soluble in water and the usual organic solvents. With concentrated sulphuric acid, it develops an eosin-red colour, with nitric acid a cherry-red, and with hydrochloric acid an insoluble red compound. The colour is discharged in all three cases by dilution with water. It dissolves in dilute sodium carbonate or sodium hydroxide, but a flocculent precipitate of the sodium salt is thrown down on the addition of excess of the reagent.

Found: N=6.4.

$C_{21}H_{15}O_3N_2As$  (418.2) requires N=6.7 per cent.

#### *7-Methyl-1:3-benzodiazole-5-arsinic Acid* (IV).

Two grams of 3:4-diamino-*m*-tolylarsinic acid were boiled with 20 c.c. of glacial formic acid for six hours. The isolation of the product was carried out as in the case of 1:3-benzodiazole-5-arsinic acid, save that the treatment with charcoal was found to be more

effective in acid solution. The air-dried product contains only traces of moisture and resembles the lower homologue very closely in its properties. It dissolves sparingly in water and crystallises in minute, prismatic needles, which darken when heated above  $280^{\circ}$  and melt and decompose at about  $300^{\circ}$  (corr.).

Found: loss at  $110^{\circ}=1.3$ .

In dried material: N=10.8; As=29.4.

$C_8H_9O_3N_2As$  (256.1) requires N=10.9; As=29.3 per cent.

*7:7'-Dimethyl-5:5'-arseno-1:3:1':3'-benzodiazole.*

This was obtained by the reduction of the above acid with sodium hyposulphite in the manner previously described (p. 1376), as a pale yellow powder, insoluble in water and the usual organic solvents, but moderately soluble in acetic acid. The corresponding *dihydrochloride* forms a pale yellow, granular powder soluble in water, but insoluble in methyl alcohol, ethyl alcohol, ether, or acetone. After drying for twenty-four hours under greatly reduced pressure, it retained solvent corresponding with two molecules of water.

Found: N=10.6; As=28.6; Cl=13.1.

$C_{10}H_{14}N_4As_2 \cdot 2HCl \cdot 2H_2O$  (521.1) requires N=10.75; As=28.8; Cl=13.6 per cent.

*2:7-Dimethyl-1:3-benzodiazole-5-arsinic Acid (VII).*

This acid was obtained by the prolonged action (six to eight hours) of boiling acetic acid on 5:6-diamino-*m*-tolylarsinic acid, the isolation being carried out in the usual manner. It is somewhat soluble in boiling water, but sparingly so in cold, and separates from the former in minute, prismatic needles which contain two molecules of water of crystallisation.

Found: loss at  $110^{\circ}=12.2$ .

$C_9H_{11}O_3N_2As \cdot 2H_2O$  requires 11.8 per cent.

In dried material: N=10.6; As=27.9, 27.5.

$C_9H_{11}O_3N_2As$  (270.1) requires N=10.4; As=27.75 per cent.

*2:7:2':7'-Tetramethyl-5:5'-arseno-1:3:1':3'-benzodiazole.*

The above acid was readily reduced to the corresponding arseno-benzene by sodium hyposulphite, under the conditions previously employed. The *arsenobenzene* closely resembles those already described in its physical and chemical properties. The *dihydrochloride* forms a pale yellow powder soluble in water, but insoluble



in the usual organic solvents. After drying for twenty-four hours in a vacuum, it retains solvent corresponding with approximately two molecules of water.

Found: N=10.0; As=27.3; Cl=12.3.

$C_{18}H_{18}N_4As_2 \cdot 2HCl \cdot 2H_2O$  (549.1) requires N=10.2; As=27.3;  
Cl=12.9 per cent.

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### CXXX.—*The Equilibrium between Carbon, Hydrogen, and Methane.*

By HUBERT FRANK COWARD and STANLEY PIERCE WILSON.

EQUILIBRIUM in the system  $C + 2H_2 = CH_4$  is more suited to experimental study, in one respect, than the more commonly investigated high-temperature dissociations, such as those of water, carbon dioxide, and hydrogen chloride. The proportion of methane in equilibrium with carbon and hydrogen diminishes with increasing temperature, and hence when equilibrium is once established in the zone of reaction, the cooling of the gaseous mixture on its removal from the carbon is not accompanied by an alteration in composition. It is a simple matter to ensure the absence of elementary carbon from any but the zone of measured temperature in which the equilibrium is attained.

The synthesis of methane from its elements was achieved by Bone and Jerdan (T., 1897, **71**, 41; 1901, **79**, 1042), who found that when a stream of hydrogen was passed over carbon at about 1200°, the resulting gaseous mixture was hydrogen containing, roughly, 1 per cent. of methane and no other hydrocarbon. This synthesis was confirmed by Bone and Coward (T., 1910, **97**, 1219), who obtained an almost theoretical yield of methane from 0.0824 gram of carbon.

The decomposition of methane into carbon and hydrogen, without the permanent formation of any detectable amount of any other hydrocarbon, was demonstrated by Bone and Coward (T., 1908, **93**, 1197).

The above-mentioned experiments, the forerunners of those now to be described, indicated that the equilibrium mixture at 1000–1200° contained, roughly, 1 per cent. of methane.

The determination of equilibrium values in the system has been

attacked in two other quarters. Mayer and Altmayer (*Ber.*, 1907, 40, 2134) carried out experiments with the aid of a catalyst at temperatures ranging from 475° to 625°, and declared that Bone and Jerdan's methane formed at 1200° could not have arisen by the direct union of carbon and hydrogen. Pring (T., 1910, 97, 498) found that a carbon rod lightly coated with platinum gave the value 0.55 per cent. of methane in equilibrium at 1200° and 0.30 per cent. at 1500°. Finally, Pring and Fairlie (T., 1912, 101, 91) conducted experiments under high pressures, and, assuming the law of mass action to hold down to atmospheric pressure, calculated the following equilibrium values:

	Amorphous carbon.	Graphite.
1200°	0.36 per cent. of methane	0.24 per cent. of methane
1500°	0.21     "     "	0.07     "     "

The series of experiments, the results of which are recorded below, were conducted in essentially the same way as those described in detail by Bone and Coward (*loc. cit.*), except that the gaseous products of reaction were passed backwards and forwards over the carbon used until analysis showed the attainment of constancy of composition. The porcelain tube used to contain the reacting substances was, as before, set up coaxially with a wider one, through which dry hydrogen was passed. The wider tube was heated electrically by means of a platinum wire resistance. The temperature of the inner tube was, at 1100°, constant, within  $\pm 6^\circ$ , for a length of 10 to 15 cm. (in different furnaces), which was ample to contain the carbon used. The latter was held in a quartz boat or in an open quartz tube just narrow enough to pass freely into the porcelain tube.

The temperature of the reaction zone was measured by means of a platinum and platinum-rhodium thermo-junction lying in the inner porcelain tube, but encased in a thin quartz tube; one wire was insulated from the other by running it through a fine quartz tube. The thermo-couple was standardised by means of lithium chloride (m. p. 605°), antimony (m. p. 628°), an alloy of 80 per cent. of copper and 20 per cent. of tin (m. p. 738°), potassium carbonate (m. p. 835°), and electrolytic copper (m. p. 1084°).

The gaseous products were collected direct from the furnace over a mixture of glycerol and water, and before being re-passed into the furnace were dried by passage through a U-tube containing fragments of dry stick potassium hydroxide.

The electrolytic hydrogen and the carbon were prepared as described by Bone and Coward. The methane was obtained by interaction between aluminium carbide and water, washed with

ammoniacal cuprous chloride and sulphuric acid, and collected after air had been displaced from the apparatus used for the preparation. Hydrogen was then removed by liquefaction of the gas by means of liquid air, and subsequent distillation. This procedure was proved to afford a satisfactory means for removing hydrogen from large volumes of methane. It cannot, however, be recommended for removing air from methane; methane must be prepared free from air in the first place unless large quantities of the gas are sacrificed during the fractional distillation after liquefaction.

*Experiments at 1100°.*

*Synthesis of Methane.*—Pure dry hydrogen was passed over 1 gram of carbon (ash, 0.06 per cent.) at the rate of about 1 litre per hour until from 5 to 6 litres of gas had been collected. A litre of this was measured and treated with palladium foil; the resulting concentrate was measured and analysed. The residual 4 to 5 litres of the gas, once passed over carbon, were re-passed at the same rate as before, and a sample was taken for analysis after concentration. The residual gas was then passed twice again over the heated carbon, and again sampled for analysis. The results of the analysis, calculated back to the unconcentrated mixtures, are (in percentages):

	1st passage.	2nd passage.	3rd passage.
Carbon monoxide .....	0.07	0.16	0.51
Methane .....	0.46	0.70	0.65
Nitrogen .....	0.21	0.51	0.67

The experiment was repeated with the same sample of carbon:

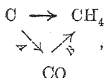
	1st passage.	2nd passage.	3rd passage.	4th passage.
Carbon monoxide .....	0.13	0.23	0.32	0.47
Methane .....	0.43	0.68	0.64	0.67
Nitrogen .....	0.26	0.49	0.56	0.69

Each experiment shows an accumulation of methane during the first and second passage of the gas over the carbon, but thenceforth the methane content remained practically constant.

The nitrogen content is a measure of the leaking in of air during the experiment and analysis, and in itself is unimportant. The carbon monoxide, due in part to air and in part to a slight oxidising action by the glaze of the heated tube, raises the question as to whether carbon monoxide may play some important part in the synthesis. It is just conceivable, although contrary to the results of other investigations,\* that carbon monoxide would be

\* Bone and Coward (T., 1908, 93, 1987) showed that when a mixture of 98 per cent. of hydrogen and 2 per cent. of carbon monoxide was passed through a porcelain tube at 1100° in the absence of carbon, no more than 0.03 per cent. of methane was present in the issuing gas.

reduced by the large excess of hydrogen present to methane and water; the latter would regenerate carbon monoxide by reaction with carbon. If carbon monoxide acted as a catalyst in the synthesis, then the two reactions—whatever they might be precisely—indicated as *A* and *B* in the scheme



would each be fast in comparison with the rate of the direct synthesis. Hence the accumulation of carbon monoxide exhibited in the experiments would only be possible provided that the reversion of methane to carbon and hydrogen were a very rapid reaction indeed when the methane was increased above about 0.7 per cent. That this is not the case is shown by experiments (below) on the decomposition of methane at 1100°. The carbon monoxide is therefore produced as a side reaction between carbon and water vapour, and plays no part in the formation of at least the great proportion of the methane found.

*Decomposition of Methane.*—A mixture containing 2.0 per cent. of methane and 98.0 per cent. of hydrogen was passed over the same sample of carbon, eight times in all. The gas was sampled from time to time for analysis as before. The results were (in percentage):

	2nd passage.	5th passage.	8th passage.
Carbon monoxide .....	0.45	0.65	0.92
Methane .....	1.18	0.64	0.61
Nitrogen .....	0.49	0.52	1.04

Here, again, the steady formation of carbon monoxide is evident, whilst the methane-content becomes constant at or before the fifth passage, and shows the attainment of equilibrium, as in the synthetic experiments.

*Synthesis and Decomposition of Methane in the Presence of Nickel.*—One gram of the pure carbon was intimately mixed with 1 gram of nickel oxide, obtained by igniting the nitrate, and the mixture heated to 300° in hydrogen until no more water vapour was formed, and then raised gradually to 1100° in a current of hydrogen. The gas issuing from the tube was collected and re-passed three times; analysis showed it to contain: carbon monoxide=1.29, methane=0.61, nitrogen=0.49 per cent.

The decomposition of methane was conducted with a mixture containing 5.7 per cent. of methane and 94.3 per cent. of hydrogen. After five passages over the same mixture of carbon and nickel, the gas contained: carbon monoxide=1.27, methane=0.57, nitrogen=

1.33 per cent. The increase in carbon monoxide is ascribed to the well-known difficulty of reducing finely divided nickel oxide completely in hydrogen.

*Collection of Results at 1100°.*—The equilibrium values indicated above are:

	Pure carbon.	Carbon-Nickel mixture.
Synthesis .....	(i) 0.65; (ii) 0.67	0.61
Decomposition .....	0.61	0.57

The mean value for the equilibrium amount of methane at 1100° is therefore 0.62 per cent.

#### *Experiments at 1000°.*

*Synthesis of Methane.*—The synthesis of methane from the highly purified carbon used in the experiments at 1100° proved to be too slow for the attainment of equilibrium at 1000°. A less pure sample containing 0.5 per cent. of incombustible matter (silica) gave the following percentage results in an experiment conducted in a similar manner to the corresponding experiment at 1100°.

	1st passage.	2nd passage.	3rd passage.	4th passage.
Carbon monoxide .....	0.05	0.10	0.17	0.28
Methane .....	1.06	0.97	0.96	1.06
Nitrogen .....	0.15	0.44	0.32	0.31

Equilibrium is evidently established from the first. The carbon monoxide-content is much lower than in the experiments at 1100°, and although increasing throughout, has no appreciable influence on the methane-content of the gases. The high value for nitrogen in the second experiment is most probably due to a small in-leakage of air during the concentration of the sample of gas analysed.

An experiment with 1 gram of carbon containing 4 per cent. of platinum, finely disseminated, gave similar values:

	1st passage.	2nd passage.
Carbon monoxide .....	0.07	0.16
Methane .....	1.09	1.08
Nitrogen .....	0.09	0.19

*Decomposition of Methane.*—A mixture containing 2.0 per cent. of methane and 98.0 per cent. of hydrogen gave in two separate experiments:

	First experiment.		Second experiment.
	3rd passage.	5th passage.	2nd passage.
Carbon monoxide .....	0.19	0.41	0.55
Methane .....	1.16	1.13	1.06
Nitrogen .....	0.83	0.84	0.69

*Synthesis and Decomposition of Methane in Presence of Nickel.*

—The same sample of a carbon-nickel mixture as was used for the experiments at  $1100^{\circ}$  gave the following results at  $1000^{\circ}$ . Starting with pure hydrogen, samples of the unconcentrated gases showed on analysis an approximately constant content of methane from the second to the sixth passages. The methane then present was determined accurately after concentration of the mixture: carbon monoxide=2.2, methane=1.23, nitrogen=0.7 per cent. The decomposition of a 3.7 per cent. methane mixture gave, in similar circumstances, a constant content of methane from the third to the seventh passage. The final composition was: carbon monoxide=1.1, methane=1.18, nitrogen=1.2 per cent.

*Collection of Results at  $1000^{\circ}$ .*—The equilibrium values indicated above are:

	Carbon (0.5 per cent. of ash).	Carbon-4 per cent. of platinum.	Carbon-Nickel.
Synthesis .....	1.01	1.09	1.23
Decomposition .....	1.13; 1.06	—	1.18

The mean value for the equilibrium amount of methane at  $1000^{\circ}$  is therefore 1.12 per cent.

*Experiments at  $850^{\circ}$ .*

The reaction between carbon and hydrogen proved to be too slow at  $850^{\circ}$  for equilibrium to be reached at that temperature within a reasonable period of time in the apparatus employed. Experiments with the nickel-carbon mixture were more successful. Synthetic experiments with a slow stream of gas showed that from the sixth to the eighteenth passage the methane content remained constant, according to the approximate results of analyses of unconcentrated samples of the mixture. The methane present at the end of the eighteenth passage was determined after concentration: carbon monoxide=0.5, methane=2.60, nitrogen=1.3 per cent. Corresponding experiments on the decomposition of methane, carried out with a very slow stream of gas, showed constant composition between the second and fifth passages of the gas: carbon monoxide=0.2, methane=2.4, nitrogen=0.6 per cent.

The equilibrium amount of methane at  $850^{\circ}$  is therefore 2.5 per cent.

*Experiments at  $650^{\circ}$ .*

Hydrogen and methane were separately heated for prolonged periods in contact with carbon at  $650^{\circ}$ . In no case did the analyses of the resulting mixtures indicate that equilibrium could be attained within any reasonable period of time, although attempts

were made to activate the carbon by means of finely divided nickel, (a) by grinding together nickel oxide and pure carbon and reducing in hydrogen at 300°; (b) by igniting a mixture obtained by evaporating nickel nitrate in the presence of excess of finely divided carbon, and heating finally in hydrogen at 300°; (c) by absorbing nickel nitrate in small pieces of porous porcelain, igniting, and depositing carbon by the prolonged passage of methane over the heated solid.

It is not concluded that it is impossible to prepare carbon in a sufficiently active state to attain equilibrium at this temperature, but the claim of Mayer and Altmayer (*loc. cit.*) to have succeeded at still lower temperatures is much weakened by the fact that they record no attempt to discover whether their gaseous products contained carbon monoxide. If, as it seems fair to assume, therefore, they overlooked carbon monoxide, much of their so-called methane may have had no actual existence. That there must have been carbon monoxide present in their products can scarcely be doubted in view of, first, the presence of large amounts of nitrogen, and, secondly, their use of somewhat large amounts of nickel, which, as is known, is difficult to obtain free from nickel oxide by reduction of the latter at a low temperature.

#### *Summary and Conclusions.*

The percentage composition of the equilibrium mixtures of methane and hydrogen in contact with amorphous carbon at atmospheric pressure is

	1100°.	1000°.	850°.
Methane .....	0.6	1.1	2.5
Hydrogen .....	99.4	98.9	97.5

These values will doubtless be capable of correlation by means of a thermodynamical equation, when the specific heats of the three reacting substances are known, together with the heat of formation of methane. Information as to the specific heat of methane at high temperatures is, however, wanting at present, and the heat of combustion of methane has apparently not been determined with a gas of sufficient purity. Calculation of the mean value of the latter between 850° and 1100° from the experimental values for the equilibrium, by means of the integrated form of the equation

$$\frac{d \log K}{dT} = - \frac{Q}{RT^2}$$

gives the value 18,000 calories, with a possible error of perhaps a couple of thousand calories.

In conclusion, the authors wish to acknowledge their indebtedness to assistance from the Government Grant Committee of the Royal Society, to Messrs. Johnson, Matthey and Co. for the loan of palladium, and to Mr. T. R. Bradbury, M.Sc., for valuable co-operation during one period of the work.

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### CXXXI.—*The Properties of Ammonium Nitrate.* *Part I. The Freezing Point and Transition-temperatures.*

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AMMONIUM nitrate is remarkable amongst salts both for its easy fusibility and for the fact that the salt exists in not fewer than five crystalline forms, the ranges of stability of which are marked by a series of four well-defined transition-temperatures. These different forms are conveniently named, in the same way as the various forms of iron, by Greek letters, starting with the form which is stable at the lowest temperatures.

The crystalline forms of these modifications, and the published data in reference to the transition-temperatures, are set out in the following table.

TABLE I.

#### *Changes of State in Ammonium Nitrate.*

Form of salt.	Crystalline system.	Change of state.	Transition-temperature.
Liquid	—	ε to liq.	165—166°, 165°, 168°, 165.2°.
ε	Cubic	δ to ε	127°, 124—125°, 124°, 123.5—125.5°, 125.6°, 122.6°, 126.2°, 124.0—125.6°, 125.0°, 125.2°.
δ	*Rhombohedral	γ to δ	87°, 82.5—86°, 81°, 82.5—86.5°, 82.8°, 83.0°, 86°, 85.5°, 84°, 84°, 82.26°.
γ	†Rhombic	β to γ	36°, 31—35°, 35°, 31—35°, 32.4°, 32.2°, 35.0°, 35.0°, 32.5°.
β	Rhombic	α to β	—16°, —18°.
α	Tetragonal		

\* Or tetragonal.

† Or monosymmetric.

In view of the fundamental character of these constants and of the fact that the temperatures are all easily accessible, a redetermination was made which has had the effect of fixing the freezing



point with an estimated error of a few tenths of a degree at  $169.6^{\circ}$ , whilst the three upper transition points have been determined probably within a few hundredths of a degree at  $125.2^{\circ}$ ,  $84.2^{\circ}$ , and  $32.1^{\circ}$ .

### I. *Freezing Point at $169.6^{\circ}$ .*

The difficulty of determining the correct melting point or freezing point of the salt, and the fact that values much below the correct figure have so often been recorded, arise from two characteristic properties of the salt, namely, the very great sensitiveness of the freezing point to the influence of small quantities of moisture (details in reference to which will be given in a later paper) and the tendency of the salt to retain its moisture even when attempts are made to remove it by somewhat drastic methods.

On account of these properties of the salt, we obtained in our earlier experiments a long series of concordant values for the freezing point, which were afterwards proved to be more than  $2^{\circ}$  too low. These freezing points were determined by observing the arrest of temperature which occurred immediately after crystallisation had begun in about 40 grams of the molten salt, the salt being stirred vigorously in a glass tube surrounded by an air-jacket in a bath of boiling water in order to prevent over-rapid cooling. The temperatures were measured by a thermometer graduated in fifths of a degree from  $0^{\circ}$  to  $200^{\circ}$ , and recently re-standardised to  $0.02^{\circ}$  at the National Physical Laboratory; this thermometer was of the compensated type, and the zero had remained constant within  $0.02^{\circ}$  over a period of about ten years. Two auxiliary thermometers were used to record the temperatures of the "exposed column" of mercury inside and outside the glass tube containing the salt. A series of freezing points determined in this way gave very concordant figures, the corrected values being as follows:

$166.95^{\circ}$ ,  $166.95^{\circ}$ ,  $166.90^{\circ}$ ,  $167.15^{\circ}$ ,  $167.0^{\circ}$ . Mean,  $167.0^{\circ}$ .

This was the freezing point of a sample of the salt which had been recrystallised twice from water and dried, first in a steam-oven during several hours, and then during a day and a night over sulphuric acid in a desiccator exhausted with the help of a Gaede mercury pump.

Doubt was first thrown on the correctness of these readings when it was discovered that a commercial sample of ammonium nitrate which had been dried and ground, and then re-dried in the usual way in the laboratory, gave a freezing point of  $168.8^{\circ}$ , that is, nearly two degrees higher than our best laboratory specimen of the salt. As this higher freezing point could obviously not be due

to impurities, which would tend to lower the freezing point of the salt, it could only be attributed to the fact that the drying had been accompanied by a grinding which was absent in the laboratory process of purification already described.

In order to secure equally favourable conditions in the laboratory, the purified salt was heated in a steam-oven, cooled, and crushed in a mortar, and left overnight in a vacuum desiccator, this cycle of operations being repeated three or four times. A series of freezing points of material prepared in this way gave the following figures:

169.16°, 169.14°, 169.04°, 169.05°, 169.06°. Mean, 169.09°.

The first two values were for ammonium nitrate from Hopkin and Williams, twice recrystallised; the next two are for the same sample after storing for some weeks in a desiccator over calcium chloride; the last value is for a commercial sample of Norwegian nitrate recrystallised from water and dried by the method just described. These experiments showed that the freezing point of the salt was at least 169.1°, and might be as high as 169.2° in view of the first two values recorded in the list.

A further improvement in the freezing point was effected by sealing up in an exhausted flask, connected with a bulb of phosphoric oxide, some of the salt prepared as described above. The nitrate was shaken up repeatedly to expose a fresh surface, and at the end of a week the freezing point was determined. In plotting the cooling curves for these determinations of the freezing point, two modifications were made in the practice previously adopted, namely, (i) the outer water-jacket was kept at 80° instead of 100° in order to reduce the amount of water vapour round the apparatus; (ii) the stirring of the molten salt was stopped as soon as the temperature showed signs of becoming steady, in order to reduce the loss of heat from the molten mass, and so to prolong as much as possible the horizontal arrest in the cooling curve. The freezing points determined in this way were

169.58°, 169.55°.

After three months' further drying by phosphoric oxide, no further rise of the freezing point was produced, but, on the contrary, it appeared to have receded slightly. The freezing point of the pure dry salt may therefore be placed at 169.6°. If the freezing point of the salt is expressed in whole numbers, the figure 170° is more exact than any hitherto given, since the experimental numbers recorded above are unlikely to be too high, but may still be slightly below the true maximum figure.

The drying of ammonium nitrate, which is not really a difficult

operation when dealing with the solid salt, cannot be effected merely by stronger heating, since the salt, which begins to decompose at  $200^{\circ}$ , retains even at this temperature the moisture produced by decomposition. Thus, two samples, which had been heated to vigorous effervescence at  $225^{\circ}$ , froze at  $166.8^{\circ}$  and  $167.0^{\circ}$  when cooled again to the freezing point of the molten salt. Again, a sample of the nitrate which melted originally at  $169^{\circ}$ , froze at  $165.5^{\circ}$  after being heated to  $230^{\circ}$  to  $240^{\circ}$  for a few minutes, and at  $163.4^{\circ}$  after a second heating. The molten salt, indeed, appears to cling to its water quite as tenaciously as concentrated sulphuric acid, and it is only by grinding the solid to a fine powder that complete drying is readily effected.

## II. *Transition-temperature at $125.2^{\circ}$ .*

When the molten salt is allowed to cool from the melting point in a tube provided with a thermometer dipping into the salt, the highest of the transition-temperatures referred to in table I gives rise only to a retardation of cooling at about  $125^{\circ}$ . In order to produce slower cooling and to secure, if possible, a horizontal arrest in the cooling curve, in spite of the poor thermal conductivity of the salt, the following method was adopted. About 90 grams of the purified salt were melted and poured into a small beaker, which was lowered into the centre of a vacuum-jacketed cylinder. A standard thermometer was inserted, and the salt was allowed to set round the bulb. The stem of the thermometer passed through a large rubber stopper, which served to close the top of the cylinder and so prevent loss of heat by convection to the outer air. The cylinder, in its turn, was immersed as far as possible in a bath of hot water, stirred mechanically, and maintained at a fairly constant temperature by a flame. A Bunsen valve was provided for the escape of air by expansion from the cylinder, whilst two auxiliary thermometers gave the temperatures of the "exposed column" of the standard thermometer. An attempt was made to retard the cooling still further by exhausting the air from the interior of the cylinder, but this procedure did not appear to serve any useful purpose, and was abandoned, because of the additional trouble caused by the frothing up of the salt to a porous mass during exhaustion. When observing the transition point at  $125^{\circ}$ , the temperature of the outer water-bath was maintained at  $95^{\circ}$ , but it was then generally allowed to cool to  $75^{\circ}$  in order to observe the further transition at  $84^{\circ}$ , to which reference is made in Section III below. The readings obtained in this way with air in the vacuum cylinder were  $125.2^{\circ}$ ,  $125.6^{\circ}$ ,  $125.8^{\circ}$ ,  $125.1^{\circ}$ ,  $125.6^{\circ}$ ,  $125.2^{\circ}$ , whilst

with the air exhausted from the cylinder the readings were  $125.2^{\circ}$  and  $125.4^{\circ}$ . The mean of the whole series is  $125.4^{\circ}$ . Zawidzki (*Zeitsch. physikal. Chem.*, 1903, **47**, 721) obtained a mean value of  $125.0^{\circ}$  for arrests in the cooling of ammonium nitrate, alone and mixed with silver nitrate.

In the case of the transition point at  $84^{\circ}$ , the poor conductivity of the salt may be compensated by stirring the powder in a small revolving drum heated externally by means of a vapour-jacket, but this method cannot be employed at the higher temperatures, as the powder begins to cake into tough lumps. A much more effective method of securing good conduction during heating and cooling consists in stirring the powdered salt in a bath of liquid not differing too widely from it in density. The liquid selected for this purpose was a mixture of tribromoethane (D  $2.62$ ; b. p.  $188^{\circ}$ ) and xylene (D  $0.86$ ; b. p.  $140^{\circ}$ ), the density of ammonium nitrate at this temperature being about  $1.6$ . Good results were also obtained by using nitrobenzene (D  $1.22$ ; b. p.  $211^{\circ}$ ). This method of improving the thermal conductivity has the advantage that the thermometric measurements can be made within a maximum of accuracy. The procedure was as follows. The liquid was made into a "mush" with powdered ammonium nitrate in a glass tube 20 cm. long and 3.7 cm. in diameter, provided with a stirrer and a split cork to carry a standard thermometer; as before, two auxiliary thermometers were used to record the temperature of the "exposed column" of mercury. The glass tube was surrounded by a metal cylinder 20 cm. long and 5 cm. in diameter, closed at the top with cotton wool, and forming a narrow air-jacket round the tube. This cylinder was supported by a bung in the axis of a larger metal cylinder, 32 cm. long and 10 cm. in diameter, containing paraffin of high boiling point to serve as a heating or cooling bath, and provided also with a thermometer. In plotting a heating or cooling curve, the paraffin bath was adjusted by hand to a temperature a few degrees above or below the transition point. The "mush" in the inner tube was stirred at intervals of thirty seconds to two minutes, according to the velocity of heating or cooling, and the thermometer was read immediately after.

The arrest-temperatures observed in this way during heating and cooling, together with the conditions under which the heating and cooling were carried out, are shown in table II.

TABLE II.

*Arrest-temperatures of Ammonium Nitrate suspended in a bath of Liquid.*

Arrest-points (corrected).	Temperature of outer bath.	Composition of liquid.
Heating: 125.21	130°	Nitrobenzene.
125.16	140	Xylene and ethylene bromide.
125.38	140	Xylene and ethylene bromide.
125.22	130	Xylene and tribromoethane.
125.25	130	Nitrobenzene.
Mean 125.24°		
Cooling: 125.27°	120°	Xylene and ethylene bromide.
125.21	120	Xylene and ethylene bromide.
125.09	120	Xylene and tribromoethane.
Mean 125.19°		

These values may be compared with those given by Vogt (*Physikal. Zeitsch.*, 1911, 12, 1129), who obtained with a dilatometer the upper and lower limits 125.25° and 125.13°, mean 125.2°. The eight values now recorded range from 125.09° to 125.38°. The mean of the five readings obtained by heating the salt is 125.24°, whilst the mean of the three readings obtained by cooling is 125.19°. The general mean of all the readings is 125.22°, and this is probably the best value for the transition-temperature. In view, however, of the difficulty of reading the temperatures to 0.01°, we prefer to give the transition-temperature to a tenth of a degree at 125.2°.

### III. Transition-temperature at 84.2°.

The transition at 84° is accomplished by an abrupt expansion which frequently made itself manifest by fracturing the glass vessel in which a cast sample of nitrate was being cooled. There is, however, a very strong tendency for over-cooling to occur, and in many cases the salt was cooled to 32° without any indication that this change of crystalline form had taken place. In order to ensure the conversion of the  $\delta$ - into the  $\gamma$ -form, it was necessary to inoculate the surface of the block with particles of the salt which had been heated to 60°, and to assist the conversion by scratching the surface with a sharply pointed glass rod. Even under these conditions, the over-cooling was usually very pronounced; the change of crystalline state (even in the vacuum-jacketed apparatus used successfully to record the change of state at 125°) only began when the temperature had fallen to 82° or below, and the latent heat was then not sufficient to restore the temperature to the transition point or to produce a horizontal arrest in the cooling curve. In

every case, therefore, the transition merely produced a sinuous curve, the highest temperature recorded for the maximum on this curve being  $82.7^{\circ}$ .

The first well-marked arrest of temperature at the transition point was observed when heating a sample of the powdered salt in a machine in which the nitrate was thrown over and over in such a way that the bulb of a thermometer was constantly bathed in the falling nitrate. A small machine in which this principle was embodied gave well-defined arrests on heating at  $84.3^{\circ}$ ,  $84.2^{\circ}$ ,  $84.3^{\circ}$ , and  $83.3^{\circ}$ , the first three values being concordant within one-tenth of a degree. It is remarkable that this transition-temperature, which was found to be so exceptionally difficult to locate by the methods first employed, proved to be by far the easiest of the transition points to determine exactly when once the proper conditions were established.

The most favourable conditions for determining this transition point were those already described in connexion with the change of state at  $125.2^{\circ}$ , namely, to compensate for the lack of thermal conductivity by stirring the powdered salt in a bath of liquid of almost equal density. The liquid used for this series of experiments was a mixture of ethylene bromide (D 2.18; b. p.  $131^{\circ}$ ) and xylene (D 0.86; b. p.  $140^{\circ}$ ). Special precautions were again needed to prevent "lag" in the change of state; the "mush" was therefore inoculated during heating with crystals heated to  $100^{\circ}$ , and during cooling with crystals heated to  $60^{\circ}$ . The inoculation was carried out just before reaching the transition point, and was followed by gentle stirring. The arrest points recorded in this way, which are lower than the mean of Zawidzki's arrests at  $85.4^{\circ}$ , but higher than the dilatometric readings  $82.16^{\circ}$  to  $82.36^{\circ}$  of Vogt, are set out in the following table:

TABLE III.

*Arrest-temperatures of Ammonium Nitrate suspended in a Bath of Liquid.*

Arrest-points (corrected).	Temperature of outer bath.	Composition of liquid.	
Heating: $84.20^{\circ}$	$90^{\circ}$	Xylene and ethylene bromide.	
$84.16$	$90$	"	"
$84.25$	$90$	"	"
$84.20$	$90$	"	"
Mean $84.20^{\circ}$			
Cooling: $84.28^{\circ}$	Falling slowly.	Xylene and ethylene bromide.	
$84.13$	" "	"	"
$84.18$	" "	"	"
Mean $84.20^{\circ}$			

In this case, the means of the four values obtained during heating and of the three values obtained during cooling are identical. The transition point may therefore be fixed, probably within a few hundredths of a degree, at  $84.20^\circ$ , or may be given to a tenth of a degree as  $84.2^\circ$ .

#### IV. Transition-temperature at $32.1^\circ$ .

(a) *Heating and Cooling Curves.*—The transition-temperature in the neighbourhood of  $32^\circ$  is more easily observed than either of those occurring at a higher temperature, since a prolonged arrest in the neighbourhood of  $32^\circ$  can always be detected when the nitrate is cooled through this temperature; indeed, both this arrest and that at  $84^\circ$  are constantly encountered when the nitrate is handled commercially. In spite of this fact, exceptional difficulty is experienced in securing an exact determination of this transition-temperature. This difficulty was ultimately traced to the fact that over a range of about a quarter of a degree on either side of the true transition point, the velocity of change of state is so slight as to be practically imperceptible, with the result that the conversion usually takes place at a temperature definitely below the transition point on cooling and at a temperature definitely above it on heating.

Large numbers of cooling curves were plotted in order to determine this transition-temperature accurately. In some experiments only a sinuous cooling curve was obtained, but in others well-marked horizontal arrests were recorded at the following temperatures:

Cast blocks .....	$31.9^\circ, 32.0^\circ, 32.0^\circ$ .
Pressed blocks .....	$31.7^\circ, 31.5^\circ, 31.4^\circ, 31.8^\circ$ .
Loose crystals .....	$31.6^\circ$ .

Horizontal arrests were also recorded, sometimes at lower temperatures, for example,  $31.0^\circ, 29.5^\circ, 29.6^\circ$ .

Arrests during heating were always at a higher temperature, and the curves were generally of a sinuous form, rising to a maximum value before falling again to a minimum approximating to the transition-temperature of the salt. These minima in the heating curves were observed at the following temperatures:

Cast blocks .....	$33.2^\circ$ .
Pressed blocks .....	$33.8^\circ, 33.1^\circ, 33.2^\circ$ .

In one experiment in which the sample had become very much over-heated before the change of state set in, a still higher reading was obtained at  $35.3^\circ$  (compare Zawidzki, *loc. cit.*, who obtained

an average of  $35.0^{\circ}$  for seven arrests in heating ammonium nitrate alone and mixed with silver nitrate).

In view of the fact that the horizontal arrests or maxima in the cooling curves were always very much more fully developed than the minima in the heating curves, it was believed that the former could be assumed to give a correct value for the transition-temperature which was located provisionally at  $32^{\circ}$ ; actually, however, the data now quoted can only be used to prove that the transition-temperature lies within certain limits, for example, between  $32.0^{\circ}$  and  $33.1^{\circ}$ , and it was not possible to secure an absolute determination by this method in view of the fact that in no case were the arrests on heating and cooling within one degree of each other.

Attempts to secure more accurate readings of these transition-temperatures by using larger quantities of nitrate up to a kilogram resulted in failure, the conductivity of the salt being so low as to prevent the effective flow of heat from one part of the mass to another; better results were, indeed, always obtained by heating or cooling much smaller quantities of ammonium nitrate, insulated as carefully as possible, for example, in a vacuum vessel, in order to reduce the rate of heating or cooling to a minimum. A distinct improvement in the heating curves was, however, obtained, as in the case of the transition at  $84^{\circ}$ , by stirring about 700 grams of powdered nitrate in a small drum, surrounded by a steam-jacket, in such a way as to produce a constant flow of nitrate past the thermometer. By using this method, the following arrests in the heating curves were recorded:

$32.6^{\circ}$ ,  $32.75^{\circ}$ ,  $32.7^{\circ}$ ,  $32.9^{\circ}$ ,  $33.0^{\circ}$ .

These readings are definitely lower than those recorded previously when cast or pressed blocks of the nitrate were heated, but no improvement could be effected in the cooling curves, so that there still remained a gap of about  $0.6^{\circ}$  between the highest arrest on cooling and the lowest arrest on heating.

The method of stirring the powdered nitrate in a bath of liquid of equal density, which had proved so successful at the higher temperatures, was a complete failure when applied to the determination of the transition-temperature at  $32^{\circ}$ . The temperature recorded on the thermometer immersed in the liquid frequently failed to show any arrest at all. Even after inoculation, the cooling curves were extremely erratic, and only on two occasions were satisfactory arrests observed at  $31.8^{\circ}$  and at  $31.6^{\circ}$ ; on no occasion was an arrest observed in the heating curve. It may be noted, however, that Müller (*Zeitsch. physikal. Chem.*, 1899, **31**, 354) obtained a satisfactory arrest at  $32.2^{\circ}$  by cooling from  $80^{\circ}$  a mix-



ture of 100 grams of ammonium nitrate with 15 to 20 grams of water, and that this temperature lies within  $0.1^{\circ}$  of our final value for this transition point.

(b) *Experiments with the Dilatometer.*—The unexpected difficulties which were encountered in trying to determine the exact position of the transition-temperature at  $32.1^{\circ}$  can be traced to the relative slowness with which the change of state takes place immediately above or below the transition point, even when assisted by inoculation, as contrasted with the much greater velocity of the changes at  $84^{\circ}$  and  $125^{\circ}$ .

This is in accordance with the general rule that changes of this character become more and more sluggish as the temperature falls, by reason of the decreasing mobility of the molecules and the increasing resistance which the rigidity of the material opposes to molecular rearrangement. Under such conditions, the thermal method becomes difficult or impossible, and it is usually necessary to fall back on some method of determining the transition-temperature in which ample time can be allowed for the change of state to reveal itself. In the case of ammonium nitrate, the most promising method was to follow, by means of a dilatometer,\* the expansion or contraction which accompanies the change of state, instead of relying on the absorption or liberation of latent heat to produce an arrest in the heating or cooling of the salt.

Experiments which were made on these lines gave us our first trustworthy value for this transition-temperature, and also provided valuable information as to the velocity of the change in the immediate neighbourhood of this point.

The solid used in the dilatometer was made by fusing pure, dry ammonium nitrate, pouring into a mortar, breaking the cast lump into pieces about 0.3 cm. in diameter, and sieving to free it from dust. This form of the salt was used in order to secure good thermal contact between the solid and liquid, and, at the same time, to avoid the risk of fracturing the bulb by the sudden expansion of a closely-packed powder. The dilatometer held about 60 c.c., and the bulb was sealed off after filling about three-quarters full with fragments of nitrate. The liquid was a paraffin of high boiling point which had been treated with concentrated sulphuric acid to free it from olefines, and then dried over metallic sodium; it was introduced in an air-free condition by making use of the apparatus shown in Fig. 1 of a paper by Wade and Merriman (T., 1912, 101, 2430).

In a dilatometer filled in this way, there are at the transition-

\* Compare van't Hoff, *Zeitsch. physikal. Chem.*, 1895, 17, 130, and "Vorlesungen," 1898, vol. i., p. 18.

temperature two alternative positions for the meniscus; one, which may be called  $V\beta$ , is the position when all the nitrate is still in the stable low temperature or  $\beta$ -form; the second, which may be called  $V\gamma$ , is the position to which the meniscus rises when all the nitrate has been converted (without change of temperature) into the lighter  $\gamma$ -form. The position  $V\beta$  can be determined by heating the dilatometer from the atmospheric temperature to a point just below the transition point;  $V\gamma$  can be determined by heating the dilatometer, say to  $50^\circ$ , until the whole of the nitrate has passed into the  $\gamma$ -form, and then cooling it to a point immediately above the transition point at  $32^\circ$ ; very little extrapolation is then required to give the exact position of these two points.

In using this method to determine the transition-temperature of ammonium nitrate, it is essential that the dilatometer should contain both forms of the salt, in order that change of state may take place quite readily in either direction. This condition was secured by heating the dilatometer to  $50^\circ$ , when the meniscus rose to a point well above  $V\gamma$ ; on immersing the dilatometer in cold water, part of the salt reverted from the  $\gamma$ - to the  $\beta$ -form, a change which was revealed at once by the appearance of white patches on the lumps of nitrate; this change took place long before the contents of the bulb as a whole had time to cool to the transition-temperature. Having made sure in this way that the nitrate in the bulb contained a substantial proportion both of the  $\beta$ - and of the  $\gamma$ -forms of the salt, it was possible to find a range of temperatures (just above the transition point) at which the meniscus tended to settle down in the neighbourhood of  $V\gamma$  by reason of the complete conversion of the contents to the  $\gamma$ -form, and a range of temperatures (just below the transition point) at which the meniscus would settle down in the neighbourhood of  $V\beta$ , owing to the complete conversion of the nitrate to the  $\beta$ -form.

The actual behaviour of the dilatometer when heated at different temperatures after the preliminary treatment described in the preceding paragraph was as follows:

(i) When the dilatometer was immersed in a thermostat at  $32.2^\circ$ , the meniscus settled down very quickly to a definite position between  $V\beta$  and  $V\gamma$ , and during the course of two hours showed no tendency to rise to  $V\gamma$  or to fall towards  $V\beta$ . The change of state appeared, in fact, to be arrested at the point to which it had been brought by the more drastic preliminary treatment of the salt. A precisely similar behaviour was observed at  $32.1^\circ$ ,  $32.0^\circ$ ,  $31.9^\circ$ ,  $31.8^\circ$ , and  $31.7^\circ$ .

(ii) When the temperature of the thermostat was reduced to  $31.6^\circ$ , the meniscus for the first time began to show a tendency to

fall towards  $V\beta$ , although the change at this temperature was so slow as to be almost imperceptible; on repeating the experiment with the thermostat set to  $31.5^\circ$ , however, a definite movement towards  $V\beta$  could be seen. These two temperatures are therefore definitely below the transition point of the nitrate.

(iii) When, on the other hand, the temperature of the thermostat was raised to  $32.3^\circ$ , a definite but exceedingly slow upward movement of the meniscus towards  $V\gamma$  was observed, and a more pronounced movement when the temperature was raised to  $32.7^\circ$ .

These experiments, on account of the extreme sluggishness of the change of state in the immediate neighbourhood of the transition point, failed to fix the exact position of this temperature, although they served to locate it between  $31.6^\circ$  and  $32.3^\circ$ . These two limits agree quite closely with those arrived at from a study of the cooling and heating curves, which had shown arrests below and above two corresponding limits at  $32.0^\circ$  and  $32.6^\circ$ ; rather closer limits were recorded by Vogt, who observed equal and opposite slow changes of volume at  $32.40^\circ$  and  $32.62^\circ$ .

(c) *Quantitative Experiments with the Dilatometer.*—In order to determine the exact position of the transition point, a series of quantitative experiments was made on the velocity of the change of state as shown by observations with the dilatometer at temperatures above and below the transition-temperature.

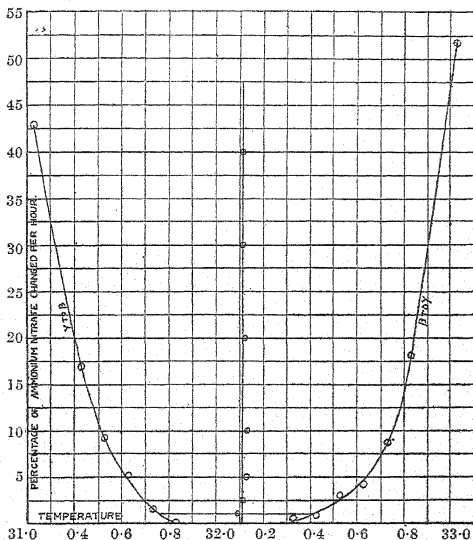
The preliminary treatment of the nitrate was much the same as in the previous experiments, and was carried out as follows. The two extreme positions of the meniscus at the transition-temperature were first located on the scale of the dilatometer, as follows:

$$V\beta = 20 \text{ cm.}; V\gamma = 48 \text{ cm.}$$

Starting with cold nitrate in the  $\beta$ -form, the dilatometer was next immersed in a bath of water at  $34^\circ$  in order to initiate the change from the  $\beta$ - to the  $\gamma$ -form. At this temperature (on account of thermal expansion), the two extreme positions of the meniscus would be about 22 and 50 cm.; when, therefore, the meniscus had risen to about 36 cm. on the scale of the dilatometer, it was clear that the two forms were present in roughly equal quantities, whilst the thermal conditions of the dilatometer and its contents had not been seriously disturbed.

After this preliminary treatment, the dilatometer was immersed in a thermostat set to a definite temperature just above or below the transition point. Thermal equilibrium was quickly established, and exact measurements could be made of the rate of movement of the meniscus consequent on the change of state from

$\beta$  to  $\gamma$ , or vice versa; the uniformity of this movement, over considerable periods of time, was such as to justify the view that the rates recorded in heavy type in table IV are definite physical constants of the change of state over the range of temperatures from  $31.2^{\circ}$  to  $33.0^{\circ}$ . The readings represent the movement in mm. of the meniscus during successive intervals of ten minutes. The mean steady velocities (obtained by averaging the numbers which are shown in heavy type in table IV) are recorded in similar units.



The final column shows the percentage of the salt which would undergo change of state in one hour, as deduced from the volume changes recorded in the previous columns. The thermometer readings are given to tenths of a degree, but are all subject to a correction of  $+0.03^{\circ}$ . It is remarkable that at temperatures a whole degree above or below the transition point, nearly an hour is required to change half of the material from the  $\beta$ - to the  $\gamma$ -form, or vice versa.

When all these velocities are plotted out in a diagram, as in

the figure, a curve is obtained which is almost symmetrical on either side. According to the well-known principle which is used in determining the "critical volume" of liquids and vapours, the transition-temperature may be determined accurately by ruling a series of horizontal lines across the velocity diagram, reading off the temperatures given by the intercepts of these lines with the curve, and working out an average value for each pair of temperatures. These averages, as set out in table V below, are as follows:

32.09°, 32.11°, 32.13°, 32.13°, 32.12°, 32.11°, 32.11°.

The mean value, 32.11°, is much more accurate than any of the values deduced either from arrests in the heating and cooling curves of the salt or from merely qualitative observations with the dilatometer, and is probably correct to within a few hundredths of a degree. For practical use, the second decimal may be omitted, and the transition-temperature given to one-tenth of a degree as 32.1°.

(d) *Form of Velocity Curve.*\*—Whilst the use of the dilatometer in determining transition-temperatures has been a well-known standard method for more than twenty years, and has been applied repeatedly when the change of state is too slow to be followed by the thermal method (see especially E. Cohen's experiments on the allotropy of metals); the complete velocity curve shown in the figure does not appear to have been plotted in any of these cases. The most striking feature of this curve is its complete symmetry, as proved by the constancy of the temperatures shown in the last column of table V, which only vary over a range of  $\pm 0.02^\circ$ . This complete symmetry, which could not be predicted, makes it possible to locate the transition temperature very accurately, and it is doubtful if any other method is capable of giving equally exact results; for comparison, it may be noted that the use of the "rectilinear diameter" to determine critical volumes depends on the existence of a skew-symmetry only in the curve of specific volumes for the liquid and saturated vapour.

In view of the regularity of the curve it is of interest to inquire into its mathematical form. The data now recorded can be expressed by the equation

$$\pm(t - t_0) = \log_{10}(\sqrt{v} + 1),$$

where  $t$  = temperature,

$t_0$  = transition temperature,

$v$  = velocity of change (percentage changed per hour).

\* Added 6/12/19.

The agreement of this formula with the experimental results is shown in the following table:

$v.$	$\pm(t-t_0)$	$\pm(t-t_0)$
	obs.	calc.
1	0.33°	0.30°
2.5	0.41	0.41
5	0.50	0.51
10	0.62	0.62
20	0.72	0.74
30	0.79	0.81
40	0.86	0.86

(e) *Anomalies in the Heating and Cooling Curves.*—At a very early period in the investigation, it was noticed with some surprise that very steady arrests of heating and cooling might occur at temperatures which were obviously not exact transition points, since they were scattered over a considerable range on either side of a mean value, which could be regarded provisionally as the correct transition-temperature. This was an anomaly for which no explanation could be suggested at the time.

General experience in such matters has shown that when dealing with rapid transitions, such as are observed in iron at 895° and 766°, the arrest in the cooling curve becomes blurred whenever liberation of latent heat fails to compensate for loss of heat by cooling; a lowered arrest point is therefore nearly always revealed by its sinuous character. In dealing with ammonium nitrate, many sinuous arrests have been observed at temperatures either below or above the real transition point, but in several cases the arrests recorded at these lower or higher temperatures were perfectly sharp.

These observations can all be interpreted in the light of the data now given for the velocity of change of state. Thus, in the first place, it is obvious that since this velocity of change is imperceptible from 31.8° to 32.3°, there can be no marked liberation or absorption of latent heat and no arrest in the cooling or heating between these limits. Outside these limits of temperature, the flow of latent heat may arrest the cooling or heating, but the conditions are such that the arrest point cannot be regarded as a fixed temperature, but must be considered as a variable temperature depending directly on the rate of heating or cooling. Thus, taking the latent heat of the transition as 5.02 calories per gram, and the velocities of change of state as recorded in table IV, the temperatures of arrest for the different rates of cooling and heating shown in column 2 of table V are given in columns 3 and 4 of that table.

TABLE IV.

*Velocity of Change of State, above and below 32.1°.*

Temperature.*	Motion of meniscus, in mm. per 10 minutes.															Mean rate in mm. per 10 minutes.	Percentage changed per hour. 42.8
	33.8	25.0	20.0	21.0	—	—	—	—	—	—	—	—	—	—	—	20.0	
31.4	8.4	9.0	8.3	8.2	8.1	7.5	7.5	—	—	—	—	—	—	—	—	7.9	16.9
31.5	11.0	2.1	2.2	3.0	3.7	4.2	4.5	4.5	4.3	4.7	4.3	4.0	—	—	—	4.3	9.2
31.6	1.4	1.2	1.9	1.9	2.0	2.2	2.5	2.4	2.4	2.4	2.3	—	—	—	—	2.4	5.2
31.7	0.8	0.8	0.4	0.4	0.7	0.7	0.6	0.7	0.6	0.6	0.6	0.6	—	—	—	0.64	1.4
31.8	10.5	1.1	0.3	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
32.0	—	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
32.2	6.5	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
32.3	7.0	1.2	0.3	0.7	0.3	0.2	0.3	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.2	0.23	0.5
32.4	—	1.7	1.6	0.1	0.4	0.2	0.2	0.3	—	—	—	—	—	—	—	0.30	0.7
32.5	13.7	4.7	3.0	2.3	2.2	1.7	1.5	1.5	1.4	1.4	1.2	1.2	—	—	—	1.4	3.0
32.6	4.8	7.6	3.5	2.3	2.8	2.5	2.0	1.7	1.9	1.7	1.6	—	—	—	—	1.9	4.1
32.7	9.0	7.9	7.0	5.7	5.0	4.8	4.0	4.0	4.0	4.0	—	—	—	—	—	4.0	8.6
32.8	†8.4	†8.0	†7.7	†7.2	†7.2	†7.2	†6.8	†6.8	†6.4	†6.3	†6.6	†6.6	†6.6	†6.6	†6.6	8.4	18.0
33.0	21.7	22.9	23.8	24.3	24.4	24.1	—	—	—	—	—	—	—	—	—	24.1	51.7

\* Correction at each temperature = + 0.03°.

† 8 minute intervals.

TABLE V.

*Velocity of Change of State of Ammonium Nitrate at Different Temperatures.*

Per cent. changed per hour.	Rate of cooling or heating. Calories per gram per hour.	Temperature (arrest-points).		Average temperature.
		Cooling.	Heating.	
1	0.050	31.75°	32.42°	32.09°
2.5	0.126	31.69	32.52	32.11
5	0.251	31.63	32.63	32.13
10	0.502	31.51	32.75	32.13
20	1.00	31.40	32.84	32.12
30	1.51	31.32	32.90	32.11
40	2.01	31.25	32.96	32.11
Mean				32.11°

The arrest points shown in the table are the temperatures at which the latent heat, liberated by a change of state proceeding with known velocity, would exactly balance the heat gained or lost by radiation, conduction, etc. Imperfect conduction of heat in the mass may displace these temperatures still further from the true transition point, and at the same time destroy the sharpness of the arrests. The latter phenomenon is observed also in the transitions at 84° and at 125°, where sinuous arrests at abnormally low temperatures are frequently observed, but the velocity of change of state at these two points is so much greater that a prolonged or "horizontal" arrest has never been observed, except at a temperature agreeing very closely with one or other of these transition points.

#### *Summary.*

(1) The freezing point of ammonium nitrate is very sensitive to the influence of traces of moisture; by careful purification and drying it has been raised to 169.6°.

(2) The highest of the transition points has been determined from the arrests of temperature on heating and cooling the salt when suspended in a liquid of similar density. The temperatures recorded were: on heating, 125.24°; on cooling, 125.19°; mean value, 125.2°.

(3) The second transition point was determined by the same method, the observed temperatures being: on heating, 84.20°; on cooling, 84.20°; mean value, 84.2°.

(4) The lower transition point cannot be determined in this way, as the change of state is too slow to be detected over the range from 31.8° to 32.2°. It was determined dilatometrically by measuring the rate of change over a range of temperatures; the



curve of velocities proved to be symmetrical, and the transition-temperature was therefore found by taking the average of pairs of temperatures at which the change proceeded with equal velocities in opposite directions. In this way, the transition-temperature was fixed at  $32.1^{\circ}$ .

(5) The form of the velocity curve for the change of state can be expressed by the simple empirical equation

$$\pm(t - t_0) = k \log_{10} (\sqrt{v} + 1).$$

(6) The arrest points due to the change of state at  $32.1^{\circ}$  never coincide with this temperature, the arrest point being determined by the rate of loss or gain of heat. A table is given showing the temperatures of arrest on cooling or heating at fixed rates expressed in calories per gram per hour.

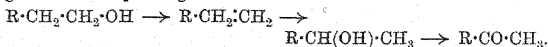
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## CXXXII.—*The Production of Methyl Ethyl Ketone from n-Butyl Alcohol.*

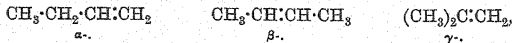
By ALBERT THEODORE KING.

IN this conversion, the usual series of steps has been employed of dehydration, re-hydration of the resulting alkylene to the secondary alcohol, and, finally, dehydrogenation of the latter to give the corresponding ketone:



No details appear to have been published hitherto regarding the hydration of butylene to the secondary alcohol, and although the first and last of the above stages have in this particular case been elsewhere described, the comparative results now obtained seem worthy of being placed on record also.

*Dehydration of n-Butyl Alcohol.*—Each of the three possible butylenes,

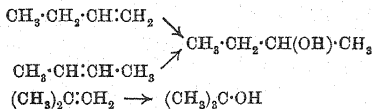


has been identified by previous observers in the product of dehydration, the composition of which would appear to depend both on the nature of the dehydrator and on the temperature employed. Thus Ipatiev (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 577), with

alumina as catalyst, at 500° obtained a gas containing 25—30 per cent. of  $\alpha$ -butylene, the rest being  $\gamma$ -butylene; the latter was attributed to the presence of isobutyl alcohol in the material employed. Senderens (*Ann. Chim. Phys.*, 1912, [viii], 25, 449), using aluminium sulphate at 300°, obtained  $\alpha$ -butylene with 27 per cent. of  $\gamma$ -butylene. Le Bel and Green obtained on dehydration with zinc chloride a product free from  $\gamma$ -butylene and containing 80 per cent. of  $\beta$ -butylene and 10 per cent. of  $\alpha$ -butylene (*Bull. Soc. chim.*, 1881, [ii], 35, 438).

In the present investigation, in which phosphoric acid on pumice was used, only slight differences were observed in the composition of the product at temperatures ranging from 280° to 400°. No  $\gamma$ -butylene was detected, and even at 280° the amount of  $\alpha$ -butylene present, so far as was indicated by fractionation of the bromide, could only be slight. This method of dehydration, therefore, yielding reasonably pure  $\beta$ -butylene, gives a much more homogeneous product than those previously described.

*Hydration of Butylenes.*—The hydration of the three butylenes with sulphuric acid should theoretically proceed as formulated below:



This conversion in the case of  $\gamma$ -butylene has been described by Butlerov (*Annalen*, 1875, 180, 245), who also records the very slow hydration of  $\beta$ -butylene, but without details of the isolation of *sec.*-butyl alcohol. Nor is the formation of the latter from  $\alpha$ -butylene recorded; and this point is under examination, the present investigation dealing only with the behaviour of  $\beta$ -butylene.

The rapid absorption of  $\beta$ -butylene (as also of  $\alpha$ - and  $\gamma$ -butylene) by concentrated sulphuric acid is well known, but by this action polymerisation, and not hydration, results. With diluted acid, the very slow action on keeping has been confirmed, but liquefied  $\beta$ -butylene, under its own pressure, agitated in contact with the acid, has been found to undergo absorption with ease. Polymerisation, which is marked at the higher concentrations, is very slight with 78 per cent. acid, and below this strength the reaction proceeds normally.

In one case, an absorption was observed of nearly 20 per cent. in excess of the butylene theoretically required to convert the acid to butylsulphuric acid, suggesting that the latter is capable of

catalysing the direct hydration of  $\beta$ -butylene. It is hoped to investigate this point further.

The diluted solution, on distillation, readily gives the secondary alcohol in good yield.

*Dehydrogenation of sec.-Butyl Alcohol.*—Reduced copper is recorded by Sabatier and Senderens as being particularly efficient in catalysing the dehydrogenation of secondary alcohols, these showing a conversion without complications, but incomplete owing to the reverse action also taking place in the presence of copper. They observed the formation from *sec.*-butyl alcohol of methyl ethyl ketone and pure hydrogen, without any accessory reaction, within the temperature range of 160–300° (*Ann. Chim. Phys.*, 1905, [viii], 4, 433, 465). In the present work, the reverse action above referred to was perceptible, but only slight.

## EXPERIMENTAL.

### *Preparation of $\beta$ -Butylene.*

The *n*-butyl alcohol distilled at 116–118°. It was gently boiled in a silica distilling flask attached to a 2.2 cm. copper tube 150 cm. in length, capable of giving, by electrical heating, temperatures, registered at the middle part, from 280° to 400°. This was packed with fragments of ignited pumice impregnated with glacial phosphoric acid. (This catalyst can be used indefinitely, its activity being renewed occasionally by burning a piece of phosphorus at the mouth of the tube, with a current of air passing through.) The unchanged alcohol and water formed were collected in a receiver with water-cooled reflux and with a syphon tube for the discharge of the condensate from time to time. The gaseous product, after scrubbing with 60 per cent. sulphuric acid to retain any  $\gamma$ -butylene, was absorbed in cooled bromine until the latter was nearly colourless. The product was then shaken with dilute alkali, dried with calcium chloride, and systematically fractionated. The following are typical results:

	(1).	(2).	(3).
Temperature .....	300–320°.	280–300°.	400°.
Dried product .....	75 grams.	114 grams.	120 grams.
<i>Final fractions:—</i>			
below 155°	(153–157°.)	3.5 "	2 "
	7 grams		
155–157°	—	9.0 "	8 "
157–159	60 "	92 "	98 "
159–161	3 "	3 "	5 "
residue	3 "	3.5 "	4 "

The boiling points of the three dibromides are:  $\alpha$ -,  $166^{\circ}$ ;  $\beta$ -, *cis*-form,  $158^{\circ}$ ; *trans*-,  $161^{\circ}$ ;  $\gamma$ -,  $149.6^{\circ}$ . Thus  $\alpha$ -butylene is not present, even at the lowest temperature employed, in notable quantity. The low fraction, possibly indicating the presence of  $\gamma$ -butylene, was not appreciably increased in (2), in which washing with 60 per cent. acid was omitted, and these lower fractions were not in sufficient quantity to detect by further fractionation the presence of  $\gamma$ -butylene dibromide. Moreover, no *tert.*-butyl alcohol was obtained from the 60 per cent. acid used to wash more than 100 grams of gas. On dilution and distillation, it yielded only 3 grams of product, which proved to be mainly *n*-butyl alcohol carried over.

Much of the butylene formed dissolves in the butyl alcohol which escapes dehydration and condenses in the receiver. From this solution, more than 150 times its volume of butylene is expelled on raising to boiling point.

No side-reaction was observed in the dehydration. The unchanged alcohol layer, dried and fractionated, yielded, finally, 1—2 per cent. distilling below  $116^{\circ}$ , the rest passing over at  $116$ — $118^{\circ}$ , and for continuous working the condensate was shaken with salt and the upper layer separated and used again, thus conserving the dissolved butylene.

#### *Action of Sulphuric Acid on $\beta$ -Butylene.*

On bubbling the gas through concentrated sulphuric acid, rapid absorption took place, the liquid becoming warm and darkening in colour. A pale yellow upper layer formed, and when this had increased to about 10 c.c. in volume, it was separated, washed, and dried with calcium chloride. It had a slight odour of hydrocarbon, and, on distilling, boiled without any constancy from  $140^{\circ}$  to  $300^{\circ}$ . The sulphuric acid layer gave, on pouring into excess of water, a turbid liquid, from which a small quantity of oil separated, which gradually darkened and became very viscous. These products, presumably formed by polymerisation of the  $\beta$ -butylene, were not further investigated. No secondary alcohol was detected in the aqueous portion.

With diluted acid, even up to 78 per cent., no appreciable absorption took place when the gas was merely bubbled through. For absorption under pressure, the following procedure was used.

The gas was liquefied by passing through a worm cooled in a mixture of ice and salt, the outlet tube dipping under the acid contained in a stout-walled bottle, also cooled in ice and salt. This gave good condensation, bubbles of gas escaping only at rare

intervals. The bottle was then closed by a rubber stopper, wired down, and, after weighing to ascertain approximately the amount of butylene condensed, shaken in a mechanical shaker until the butylene layer had disappeared. In each case, 50 c.c. of pure acid were used with varying dilution, and the time occupied for absorption was roughly noted, with the following results:

Concentration. Per cent.	Butylene. Grams.	Time taken.
100	17	—
84.0	21	5 minutes
78.0	23	20 "
76.0	22	40 "
75.3	22	1 hour
72.5	19	1.6 hours
70.0	24	5 "
64.8	10	8 "
50.0	22	Little effect after 15 hours.

With pure acid, the absorption was complete in a few seconds. On pouring into ice, an oil separated which, after drying with calcium chloride, weighed 15 grams. It distilled from 140° to above 300° without boiling constantly at any point, like the product previously described. No secondary alcohol was present in the aqueous portion.

With 84 per cent. acid, the alcohol was the main product, but considerable polymerisation occurred. Moreover, the acid crystallised in the freezing mixture, causing inconvenience through blocking of the delivery tube. The freezing-point curve shows the range of concentration, having sufficiently low freezing point and also giving normal reaction in reasonable time, to be from 74.5 (f. p. -20°) to 78 per cent. (f. p. -20°). The concentration ultimately adopted was 75 per cent. With 78 per cent. acid, a trace of oil with a terpene-like odour was observable on dilution, this becoming imperceptible with the lower concentrations.

The rise of temperature was very marked with the higher concentrations. The pressures generated by the liquid butylene were approximately determined by a pressure gauge as follows:

12°	0.6 atm.
20	0.95 "
30	1.4 "
40	1.9 "

With 75 per cent. acid, the temperature did not reach 40°, and the operation is thus without risk.

To ascertain the extent of absorption, 76 per cent. acid, containing 92 grams of pure acid, was shaken with 63 grams of butylene (theoretical quantity=51.5) for fifteen hours. The excess of gas was allowed to escape, and any in physical solution removed by

exhaustion, when 61 grams were found to have been chemically absorbed. About 90 per cent. of the theoretical quantity was, however, usually employed.

#### *Hydrolysis of Butylsulphuric Acid.*

Comparative experiments were made, using three portions of 50 grams from the same batch of butylsulphuric acid. These were respectively neutralised with sodium carbonate and treated with quantities of 50 and 25 grams of water. The liquids were distilled, and the distillates caught in graduated tubes and thoroughly shaken with salt solution and a slight excess of salt. The volumes of upper layer were 23 c.c., 23 c.c., and 22.5 c.c. respectively. With neutralisation as employed by Butlerov (*loc. cit.*), the alcohol distilled over very slowly with a large quantity of water. Distillation with the lesser quantity of water gave a distillate with only a small aqueous layer, the bulk being retained by the acid, but with a slightly lower yield, although no ether was detected in the product. Dilution with an equal weight of water was therefore adopted.

With this procedure, 51 grams of butylene yielded a distillate which, after salting out and drying with potassium carbonate, weighed 60 grams, that is, 89 per cent. of the theoretical on the crude material. From 150 grams of dried, undistilled product, after careful fractionation, were obtained as final fractions:

below 97.5°	3 grams
97.5—99.5°	131 "
99.5—100°	8 "
residue	5 "

The fraction 97.5—99.5° was employed for conversion to ketone.

#### *Dehydrogenation of sec.-Butyl Alcohol.*

The procedure followed was substantially that of Sabatier and Senderens (*loc. cit.*). A copper tube 172 cm. long and 1.2 cm. in diameter was packed with copper oxide from wire kept in place with plugs of rolled copper gauze, and enclosed in a 2.5 cm. copper tube 135 cm. long wired for electrical heating. After reduction of the wire with ethyl alcohol vapour, and expulsion of the latter, *sec.*-butyl alcohol was distilled through from a silica flask at such a rate that the distillate passed through at the rate of about one drop a second. This was caught in a receiver cooled in ice-water. The hydrogen was evolved just too fast to allow the bubbles through a wash-bottle to be counted. The temperature remained

fairly constant throughout, the fluctuation on either side of  $290^{\circ}$  being never more than  $5^{\circ}$ .

In the first preparation, from 100 grams of alcohol, 104 of distillate were obtained. This contained water, formed from some unreduced copper oxide, and, on fractionating, 94 grams distilled at  $73-75^{\circ}$ , the mixture separating a small, lower layer of water. After drying with potassium carbonate, the bulk distilled at  $79-81^{\circ}$ .

Two hundred and fifty grams of alcohol gave an almost theoretical yield of dried, undistilled product, which gave the following 'fractions':

76—79°	5 grams
79—81	199 „
81—82	9 „
82—86	6 „
residue	12 „

Thus the conversion is upwards of 90 per cent.

The fraction boiling at  $79-81^{\circ}$  decolorised permanganate, but after stirring with about half a gram of powdered potassium permanganate for a short time, the colour persisted. On distilling off and drying thoroughly with potassium carbonate (the boiling point is very easily affected by traces of water), the ketone distilled almost completely within the range  $80-80.6^{\circ}$ .

The yield on the small scale from the crude butylene is about 70 per cent. of the theoretical, and with continuous working and recoveries this figure at least should be reached in the complete synthesis from *n*-butyl alcohol.

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### CXXXIII.—*Conversion of the Simple Sugars into their Enolic and Ethylene Oxide Forms.*

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No group of compounds is more remarkable than that of the hexoses, on account of their extreme mutability. Glucose, for example, may be obtained in an  $\alpha$ - and a  $\beta$ -crystalline form, and if either of these is dissolved in highly purified water the solution is all but stable. Yet if a trace of alkali is added, an equilibrated

mixture of the two isodynamic forms is practically instantaneously produced. The change has been specially studied by Lowry (T., 1903, **83**, 1314; 1904, **85**, 1551), and its character has been discussed also by one of the authors (T., 1903, **83**, 1305).

The more gradual change, also under the influence of alkali, from one hexose into another, within sections including as many as four members of the group (for example, glucose  $\rightleftharpoons$  mannose  $\rightleftharpoons$  fructose  $\rightleftharpoons$  glucose), was brought to light through the painstaking labours of the late Lobry de Bruyn (*Rec. trav. chim.*, 1895, **14**, 156, 204). In this case, the transition has been assumed to involve the formation of an enolic form as an intermediate term. In the case of the hexoses the aldehydic form (aldehydrol) is commonly supposed to have but an ephemeral existence, and it is held that  $\alpha$ - and  $\beta$ -glucose are butylene oxide or pentaphane derivatives corresponding with the two methyl glucosides. The latter, it is well known, are simultaneously produced by the action of a strong acid on glucose dissolved in methyl alcohol; a residue, long unexplained, has recently been shown to contain a third isomeric methyl glucoside, regarded by Fischer and by Irvine as the derivatives of an ethylene oxide form of the hexose.

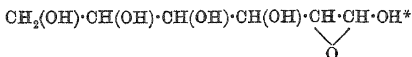
Irvine and his school (T., 1915, **107**, 524; 1916, **109**, 1305, etc.) have shown that the new methyl glucoside is characterised by its capacity to condense with acetone, to reduce potassium permanganate solutions, and to undergo auto-condensation, and that the activity of the parent glucose from which it is derived far exceeds that of  $\alpha$ - or  $\beta$ -glucose.

The observations we have to place on record relate to the changes effected in the simple sugars by acids and by alkalis, as measured both by means of the polarimeter and by means of increased liability to oxidation.

A solution of either  $\alpha$ - or  $\beta$ -glucose in water (both well purified) is practically unaffected by permanganate. In acid solution, reduction of the permanganate sets in at once and at a definite rate under definite conditions; thus, under the standard conditions detailed in the experimental part, 10 c.c. of 1 per cent. of  $\alpha$ - or  $\beta$ -glucose in *N*/10-hydrochloric acid solution decolorise 2 c.c. of *N*/100-permanganate solution at 25° in twenty-eight to thirty minutes. That the change is instantaneous is proved by the fact that the reducing power acquired is independent of the time during which the acid has acted, solutions containing acid which have been kept various times all having the same reducing power. The strength of the acid, however, is a factor in the change, the effect being less the weaker the acid and likewise the less concentrated the acid.

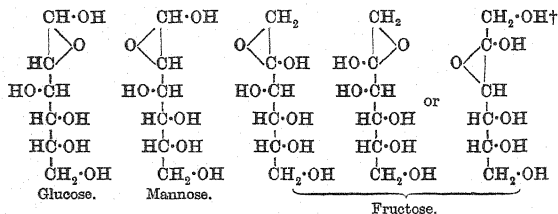


We consider that the active agent is the ethylene oxide modification of glucose,



The amount of the ethylene oxide form present is regulated by an equilibrium depending on the strength of the acid, but that it is small is shown by the fact that the optical rotatory power of glucose in an acid is the same as in an aqueous solution. The ethylene oxide form is reproduced as oxidation by the permanganate proceeds, as shown by the fact that fresh additions of permanganate solution are decolorised.

Mannose and fructose are affected by acids in a similar way, but the altered mannose solution acts far more rapidly than that of glucose; fructose is only slightly less active than mannose. For example, under precisely comparable conditions, whereas the reduction of permanganate by glucose occurs in twenty-eight to thirty minutes, that by mannose takes only from twelve to thirteen, and that by fructose sixteen to seventeen minutes.



In view of the close relation of the ethylene oxide forms of these sugars, it seems not improbable that one of the isodynamic forms is the more oxidisable, and that this is the form present in mannose.

The reduction of permanganate (as well as of methylene-blue and of indigo-blue) is also promoted by the addition of alkali. In

\* At first sight the alterations involved in the conversion of butylene oxide into ethylene oxide or enolic forms of glucose appear somewhat far reaching when viewed only in the light of the conventional structural formulæ. If, however, structural models are prepared of the sugars on the lines of the Pope-Barlow hypothesis of close packing a more rational interpretation of the changes is realised.

† This form of fructose is present in sucrose according to Haworth and Law (L., 1916, 109, 1314).

this case, however, the change of the hexose is more gradual, as, within limits, the solution is the more active the longer the alkali has acted. The interactions in the three cases take place at corresponding rates, showing that in each case the same change is being studied. Under the experimental conditions observed, the reduction phenomena correspond only with the changes in structure which take place in the course of the first few hours, and it is unlikely that any far-reaching disturbance has occurred in the carbon chain beyond the atoms 1 and 2.

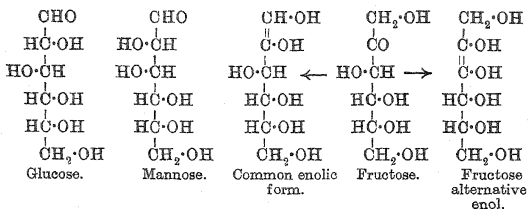
As shown by the polarimeter, the equilibrium between the  $\alpha$ - and  $\beta$ -butylene oxide forms of the sugar is established instantaneously in alkaline solution, and subsequently the optical activity falls slowly, but it is still of considerable magnitude at the end of six hours. After this, it continues to fall, some fifteen to twenty days being required before the solution loses its activity. To judge from the slowness with which alkali acts as compared with acid, taking into account the instantaneous equilibrium of the  $\alpha$ - and  $\beta$ -forms in the presence of alkali, it is clear that the latter are not concerned in the change. It therefore seems probable, so far as the effect produced by acids is concerned, especially in view of the distinctly basic character of ethylene oxide, that the ethylenic oxide form of the hexose, not an enol, is the active agent. Assuming the enol to be concerned, acids equally with alkalis should convert one hexose into another in the Lobry de Bruyn change, but this is known not to be the case.

It is noteworthy, however, that ethylene oxide itself has no reducing power on either methylene-blue or indigo-blue in alkaline solution, although it readily affects permanganate. It is by no means clear, in fact, that the action of alkali is comparable with that of acid, and it may well be that reduction is effected by the enol. Whereas possibly in acid solution a salt of the basic ethylene oxide hexose is formed, in alkaline solution the scission of all ring systems and the production of a metallic salt of the open-chain enol appears more probable.

Whilst glucose decolorised the standard amount of permanganate initially in eleven minutes (in the presence of one equivalent of sodium hydroxide), fructose takes three and mannose twenty-five minutes; the figures after the solutions have remained for five hours are, respectively, glucose 3, fructose 1.25, and mannose 9 minutes.

As the formulæ show, all three substances can give the same enolic form. On the supposition that "enol" rather than "ethylene oxide" is initially formed in the presence of alkali, the configuration represented by fructose is most, and that represented

by mannose least, prone to undergo enolisation. This is in marked contrast to the behaviour of the same three sugars towards acid.



The change in presence of alkali is qualitatively proportionate to the strength of the alkali. It is of special interest in this connexion that pyridine has a similar effect to the other alkalis. In this case, as pyridine is such a weak alkali, the sugars were dissolved in the base itself. Decolorisation of glucose took place initially in about fifty to sixty minutes, increasing to thirty minutes in about five hours, whereas with fructose the times were thirty minutes initially and eight minutes after six hours.

This observation is quite in harmony with the important part which pyridine and quinoline have played in sugar chemistry as the media in which epimeric changes are effected, causing the rearrangement of the groups attached to the asymmetric carbon atom at the end of the chain. Both in the interconversion of epimeric hexonic acids (E. Fischer, *Ber.*, 1890, **23**, 2625) and of epimeric glucosides (E. Fischer and von Mechel, *Ber.*, 1916, **49**, 2813; 1917, **50**, 711), formation of intermediate modifications must be involved.

The alterations in structure which we have followed by the changes in reducing power are clearly in no way related to those known as mutarotation. Whereas the former take place instantaneously in the presence of acid, and more slowly in the presence of alkali, mutarotation is brought about immediately in the presence of alkali and more slowly in the presence of acid.

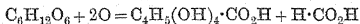
#### EXPERIMENTAL.

Reducing tests were made by withdrawing 10 c.c. of the sugar solution (generally 1 per cent., or 1/18 gram-molecule of hexose per litre, except when polarimetric comparisons were also made, in which case 5 per cent. solutions were used) into a stoppered test-tube and adding 2 c.c. of the standard permanganate or dye solution; *N*/100-potassium permanganate was invariably used, whilst

the dye solutions consisted respectively of a 0.025 per cent. solution of methylene-blue and a solution of neutral indigo sulphonates which contained 0.045 per cent. of indigotin. In those cases in which it was desired simultaneously to neutralise the acid or alkali present, special solutions of *N*/100-permanganate were employed containing respectively the amount of sodium hydroxide or of sulphuric acid per 2 c.c. necessary to neutralise the acid or alkali present in the 10 c.c. of sugar solution exactly.

The behaviour of permanganate with the sugar solutions varies considerably according to the conditions studied; thus, acid fructose or mannose solutions pass simply from pink to clear white, and perfectly definite end-points are obtainable in these cases. In other cases, generally those of slowly reducing acid media or of rapidly reducing neutral or alkaline solutions, the pink tint gives place, with varying rapidity, to a very pale yellow, and ultimately to the colourless, condition. A definite colour standard, just short of colourless, was adopted here, and sharp end-points could be obtained without difficulty. With slowly reducing neutral or weakly alkaline solutions, however, a precipitate of manganese dioxide of variable degree of fineness is apt to appear, and it is difficult to determine the precise point at which actual precipitation sets in; cases of this kind are denoted in the tables which follow by the addition of "indefinite" or "with pptn."

It is obvious that in the latter case the amount of reduction will not be so great as when the formation of the colourless manganous salt solution has occurred. In point of fact, whilst the 10 c.c. of sugar solution employed has contained 0.1 gram (1 per cent. solution) or 0.5 gram (5 per cent. solution) of hexose, the 2 c.c. of *N*/100-permanganate, assuming the action



to occur, are capable of oxidising 0.0009 gram of hexose if the reduction proceeds to the manganous state, or 0.00054 gram if the action is arrested at the stage of manganese dioxide.

In the extreme cases, therefore, we have measured the time of oxidation of 0.9 per cent. of the sugar present in the solution, whilst, on the other hand, we have dealt with the time of oxidation of as small a proportion as 0.11 per cent. or less of the sugar present.

The stock solutions of sugars, and also the portions undergoing tests, were maintained at 25° throughout.

*Neutral Solutions.*

The dye reagents are unaffected by any of the sugars tested in neutral solution. Under the conditions described, permanganate is decolorised by fructose in four or five hours, whilst with either form of glucose the solution becomes orange in about six hours, and fades to a full yellow tint after twenty-four hours. The behaviour of mannose is very similar to that of glucose. These results are obtained equally with fresh solutions and those which have remained for a day at 25°.

It may be of interest to state that if the test is conducted in *N*/10-sodium chloride solution instead of in water, precipitation of manganese dioxide sets in at a much shorter time; the figures obtained for fructose,  $\alpha$ -glucose, and mannose were respectively 93, 90, and 115 minutes.

*Acid Solutions.*

(i) *Aqueous Solutions.*—The oxidation times are constant at any age of the solution in the case of acids. This is illustrated by the figures for fructose,  $\alpha$ - and  $\beta$ -glucose, and mannose given in table I.

The dependence of the time factor on the hydron concentration is shown by the results in table II, wherein only the mean figures are quoted; it may be emphasised that the agreement of the individual readings at varying ages of the sugar solutions is in all cases as good as those given *in extenso* in table I.

Two series of times are given for each sugar, the first being for the simple acid solution; the second gives the values obtained when the test-solutions were neutralised simultaneously with the addition of permanganate.

In the case of the higher concentrations of hydrogen ions investigated, neutralisation of the acid present, effected at the same time as the addition of permanganate, does not appreciably alter the oxidation times.

At the lower concentrations of hydrogen ions, and notably with the weaker acids, such as phosphoric and acetic, the oxidation times for the "neutralised" solutions are quicker than for the acid solutions, and progressively so as the strength of the acid decreases.

The identity of the oxidation times for "neutralised" and for acid solutions with the stronger acid solutions is quite definite, and we consider that they indicate the persistence of the active form of the sugar after neutralisation of the acid has taken place; the meaning of the results with neutralised solutions of weaker acids is by no means clear, although they are explicable to a certain

extent when it is borne in mind that the sodium salts of the weaker acids will be appreciably hydrolysed, so that we have really passed over in this instance to a feebly alkaline solution of the sugar.

The age of the solution is given in hours, the first reading (0.1 hour) having been taken immediately solution was complete; in most instances, this reading was commenced about three to five minutes after the addition of acid. The times of oxidation are in minutes, unless an explicit statement to the contrary is added.

TABLE I.

*One per cent. Sugars in N/10-HCl and N/10-H<sub>2</sub>SO<sub>4</sub>.*

Age.	Fructose.		$\alpha$ -Glucose.		$\beta$ -Glucose.		Mannose.		Acid.
	Acid.	Neutd.	Acid.	Neutd.	Acid.	Neutd.	Acid.	Neutd.	
0.1	17	15	29	27	30	30	13	12	HCl
1.0	16	17	28	29	32	30	12	13	
2.0	17	18	31	28	32	27	12	12	
5.0	16	18	29	—	34	29	12	17	
0.1	31	24	52	41	—	—	25	21	H <sub>2</sub> SO <sub>4</sub>
1.0	30	26	51	43	—	—	23	20	
2.0	28	22	51	42	—	—	22	20	
5.0	30	26	53	48	—	—	24	21	

TABLE II.

*One per cent. Solutions of Fructose and  $\alpha$ -Glucose in Acids of Varying Strength.*

Acid.	Hydron concentration. Equivs. per litre.	Fructose.		$\alpha$ -Glucose.	
		Acid.	Neutd.	Acid.	Neutd.
N/10-HCl .....	0.0910	16	17	29	28
N/10-H <sub>2</sub> SO <sub>4</sub> .....	0.0660	30	24	52	43
N/50-HCl .....	0.0188	69	62*	118	97*
N/50-H <sub>2</sub> SO <sub>4</sub> .....	0.0160	76	75*	124	75*
N/10-H <sub>3</sub> PO <sub>4</sub> .....	0.0130	211	84*	238	150*
N/10-C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> .....	0.0012	280	20*	1,070	65*

\* With precipitation.

The hydron concentrations are taken from data in Landolt and Börnstein's "Physikalische-Chemische Tabellen."

(ii) *Alcoholic Solutions.*—Some observations were made in methyl- and ethyl-alcoholic hydrogen chloride solutions in view of the considerable amount of synthetic work which has been carried out in these media. Concentrations of N/20-acid were employed in order to approximate to the 0.25 per cent. hydrogen chloride solutions which have most frequently been used by E. Fischer,

Irvine, and other workers with these reagents. Very similar results were obtained to those found in aqueous solutions.

The methyl alcohol was distilled over lime and then over a little fructose, whilst the ethyl alcohol was twice distilled over lime and potassium permanganate. Ten c.c. of the neutral solvents caused precipitation in the permanganate test in six hours in the case of methyl, and in sixteen hours with ethyl, alcohol. *N*/20-Methyl-alcoholic hydrogen chloride, however, decolorised the permanganate in ninety-eight minutes, the time with *N*/20-ethyl-alcoholic hydrogen chloride being fifty-six minutes.

TABLE III.

*One per cent. Solutions of Fructose and  $\alpha$ -Glucose in Alcoholic N/20-Hydrogen Chloride.*

Solvent.	Age.	Fructose.	$\alpha$ -Glucose.
<i>N</i> /20-Methyl-alcoholic hydrogen chloride .....	0.1	7	11
	2.0	—	16
	3.0	17	—
	24.0	25	120
<i>N</i> /20-Ethyl-alcoholic hydrogen chloride .....	0.1	6	9
	2.0	7	20
	3.0	8	10
	24.0	6	23

#### *Alkaline Solutions.*

In alkaline solutions, it is also possible to utilise the reduction of the dyes indigo and methylene-blue; the former gives two fairly definite colour stages, passing from blue through green to a clear red, and then changing to pure yellow. The times occupied from the commencement of the test in reaching the standard red and yellow tints are given in the tables under the columns headed respectively "R" and "Y."

Methylene-blue fades to a colourless solution. In both cases, the dyes are restored by contact with air, and it was found desirable to fill the upper part of the test-tubes with an inert gas, hydrogen being employed.

It was found that the stock alkaline sugar solutions, whether maintained under air or under hydrogen, behaved the same towards the three oxidising agents.

The result of neutralising the alkaline sugar solution, when the latter has been freshly prepared, is to cause a very marked retard-

ation in reducing power, but after the alkaline solution has remained for some hours, the reducing power after neutralisation becomes greater, approaching that of the alkaline solution itself in about twenty-four hours.

This shows that initially the change induced by alkali is reversed on neutralisation, but the progressive alteration in behaviour is somewhat obscure, although it may well be due to the appearance of small amounts of decomposition products resulting from more profound disturbance of the sugar molecule.

It is evident, however, that the behaviour of neutralised alkaline solutions is quite distinct from that of neutralised acid solutions, so that it may be considered that the cause of the reducing activity of the sugar is not the same in each case.

The subjoined tables give the full series of readings up to five hours for fructose,  $\alpha$ - and  $\beta$ -glucose, and mannose in the presence of one and of two equivalents of sodium hydroxide (table IV). In table V are recorded the initial and final values (five hours) for fructose and  $\alpha$ -glucose with varying concentrations of sodium hydroxide, and in table VI we quote similar data for these sugars in the presence of one equivalent of a number of aqueous alkalis.

*Correlation of the Reducing Action of the Sugars with Alterations in Optical Rotatory Power.*

In order to obtain a convenient polarimetric reading in the 2-dcm. tubes employed, the behaviour of 5 per cent. solutions of fructose and of  $\alpha$ -glucose was examined in neutral, acid, and alkaline media. The concentrations of the acid ( $N/10\text{-HCl}$ ) and of the alkali ( $N/18\text{-NaOH}$ ), and the conditions of the reducing time-tests, were otherwise maintained unaltered. The alteration in concentration of the sugars involved the determination of the corresponding times of reaction with permanganate and the dyes, and the results of these and of the observations of optical rotatory power are collected in table VII.



TABLE IV.  
One per cent. Sugar Solutions with One and Two Equivalents of Aqueous Sodium Hydroxide.  
(a) Tests with Potassium Permanganate.

NaOH equiv.	Age.	Fructose.		$\alpha$ -Glucose.		$\beta$ -Glucose.		Mannose.	
		Alk.	Neutd.	Alk.	Neutd.	Alk.	Neutd.	Alk.	Neutd.
2.0	0.1	1.75	65.0*	10.0	61.0*	—	—	26	65†
	1.0	1.25	60.0*	8.0	90.0†	—	—	24	120†
	3.5	0.75	8.0	3.0	150.0†	—	—	16	150†
	5.0	0.50	0.5	2.0	60.0†	—	—	14	70
	24.0	0.75	0.2	1.75	1.25	—	—	7	13
1.0	0.1	3.00	60.0†	11.0	180.0†	15.0	35.0†	25	90†
	1.0	2.00	—	7.5	—	11.0	50.0†	20	—
	3.0	1.75	65.0	4.5	73.0*	9.0	48.0	17	73*
	5.0	1.25	11.0	3.0	48.0*	4.0	37.0	9	48*
24.0	24.0	1.25	0.25	2.5	2.5	4.5	4.5	4	5

## (b) Tests with Indigo and Methylene-blue.

NaOH equiv.	Age.	Fructose.		$\alpha$ -Glucose.		$\beta$ -Glucose.		Mannose.	
		Indigo.	Meth. Blue.	Indigo.	Meth. Blue.	Indigo.	Meth. Blue.	Indigo.	Meth. Blue.
2.0	0.1	R. 1.00	1.50	R. 4.00	7.00	R. —	—	R. 17†	29
	1.0	0.75	0.50	3.25	4.00	—	—	12†	21
	3.0	0.50	0.40	2.50	3.00	—	—	8†	15
	5.0	0.50	0.35	2.25	2.25	—	—	7†	10
	24.0	1.25	2.00	2.50	3.00	—	—	5†	6
1.0	0.1	2.25	3.00	9.0	11.0	14	18	22†	33
	1.0	1.50	1.25	6.5	7.0	8	12	19†	30
	3.0	1.25	1.00	6.0	5.0	7	9	16†	28
	5.0	1.25	1.00	5.0	4.0	5	5	17†	24
	24.0	3.25	2.00	5.0	5.5	4	4	17†	22

\* Precipitation set in.

† Indefinite end-point.

TABLE V.  
*One per cent. Solutions of Fructose and  $\alpha$ -Glucose with Varying Strengths of Sodium Hydroxide.*

NaOH equiv.	OH ion concn. per litre.	Age.	Fructose.						$\alpha$ -Glucose.					
			Indigo.			Permanganate			Indigo.			Meth. Blue.		
			R.	Y.	Meth. Blue.	Alk.	Neutd.		R.	Y.			Alk.	Permanganate.
2.0	0.0078	0.1	1.00	2.50	1.50	1.75	65.0*		4.00	6.00		7.00	10.0	61*
—	—	5.0	0.50	1.25	0.35	0.50	0.5		2.25	5.00		2.25	2.0	60†
1.0	0.0506	0.1	2.25	3.50	3.00	3.00	60.0†		9.0	12.5		11.0	11.0	180†
—	—	5.0	1.25	2.50	1.00	1.25	11.0		5.0	11.0		4.0	3.0	48*
0.75	0.0383	0.1	5.0	7.5	5.0	5.0	55.0*		14.0	21.5		19.5	16.0	57*
—	—	5.0	1.25	3.0	1.0	1.5	24.0		6.0	13.0		6.0	8.5	23*
0.5	0.0256	0.1	6.0	8.5	6.0	7.0	29.0*		20.0†	35.0		27.0	24.0	43*
—	—	5.0	3.0	4.5	3.0	3.5	19.0†		14.0†	23.0		19.0	15.0	36*
0.25	0.0129	0.1	15.0†	20.0	17.5	14.0	50.0*		51.0†	91.0		66.0	95.0†	50*
—	—	5.0	7.0†	10.0	5.0	5.0	51.0†		25.0†	50.0		25.0	33.0	31*

\* Precipitation set in.

† Indefinite end-point.

TABLE VI.  
*One per cent. Solutions of Fructose and  $\alpha$ -Glucose with One Equivalent of Various Alkalis.*

Alkali.	OH ion concn. per litre	Age.	Fructose.					$\alpha$ -Glucose.				
			Indigo.		Permanganate.			Indigo.		Permanganate.		
			R.	Y.	Meth. Blue.	Alk.	Neutd.	R.	Y.	Meth. Blue.	Alk.	Neutd.
NaOH	0.0506	0.1	2.25	3.50	3.00	3.00	60†	9.0	12.5	11.0	11.0	180†
	—	5.0	1.25	2.50	1.00	1.25	11	5.0	11.0	4.0	3.0	48†
KOH	0.0506	0.1	4.50	6.00	5.00	4.00	120†	13.0	20.0	18.0	16.0	20*
	—	5.0	0.75	2.50	0.75	1.25	60	5.0	10.0	6.0	5.0	60
Ba(OH) <sub>2</sub>	0.0478	0.1	5.00	6.00	5.00	4.00	—	15.0†	19.0	18.0	16.0	—
	—	5.0	1.00	1.50	1.25	1.25	—	4.0	6.5	5.0	4.0	—
Na <sub>2</sub> CO <sub>3</sub>	0.0024	0.1	†	83.0	150.0	30.0†	61*	Practically unchanged.				
(Hydrolysis)	5.0	5.0	†	56.0	98.0	16.0	20*					
K <sub>2</sub> CO <sub>3</sub>	?	0.1	†	57.0†	88.0†	42.0†	39*	Practically unchanged.				
(Hydrolysis)	5.0	5.0	†	49.0†	60.0	27.0	27*					
NH <sub>4</sub> OH	0.0011	0.1	Very little action.					Practically unchanged.				
	—	5.0										
						70.0	19*				150.0†	31*
						48.0	60†				Indef.	40*

\* Precipitation set in. † Indefinite end-point.

TABLE VII.  
*Comparison of Rotatory Power with reducing Action of Sugars in 5 per cent. Solution.*  
 (a) *Neutral Solutions.*

Age in hours.	Fructose.			Glucose.			$\beta$ -Glucose.		
	Permanganate.	$[\alpha]_D$ .		Permanganate.	$[\alpha]_D$ .		Permanganate.	$[\alpha]_D$ .	
0.1	24 hours. Almost colourless	-104.2°		23 hours. Still yellow	+96.8°		6 hours. Almost colourless	+27.5°	
0.5	—	92.5		—	—		—	33.8	
1.0	24 hours. Almost colourless	91.5		22 hours. Still yellow	68.2		6 hours. Pale yellow	37.8	
2.0	24 hours. " "	91.2		—	—		—	44.5	
3.0	—	—		—	—		—	—	
3.5	—	—		22 hours. Still yellow	52.0		—	—	
4.0	—	91.2		—	—		20 hours. Clear.	49.2	
5.0	—	—		—	51.5		—	49.2	
6.0	—	91.2		—	—		—	49.0	
24.0	48 hours. Almost colourless	91.2		Clear before 24 hours.	50.7		Clear before 24 hours.	49.5	

TABLE VII. (continued).  
(b) Solutions in N/10-Hydrochloric Acid.

Age in hours.	Fructose.				Glucose.				$\beta$ -Glucose.			
	Permanganate.		[ $\alpha$ ] <sub>D</sub> .	Neutd.	Permanganate.		[ $\alpha$ ] <sub>D</sub> .	Neutd.	Permanganate.		[ $\alpha$ ] <sub>D</sub> .	Neutd.
	Acid.	Neutd.			Acid.	Neutd.			Acid.	Neutd.		
0.1	8	8	-91.2°	—	21	21	+91.8°	—	13	16	+30.5°	—
0.5	—	—	91.5	—	—	—	—	—	—	—	43.5	—
1.0	8	6½	91.5	—	21	20	51.2	—	13	14	49.8	—
2.0	7	6½	91.0	—	—	—	—	—	—	—	—	—
3.0	—	—	—	—	—	—	—	—	12½	29	49.5	—
3.5	—	—	—	—	18	20	49.8	—	—	—	—	—
4.0	7½	8	91.0	—	—	—	—	—	—	—	49.5	—
5.0	—	—	—	—	17	16½	49.8	—	13	25	49.5	—
6.0	—	—	90.8	—	—	—	—	—	—	—	—	—
24.0	8	10	90.8	—	20	14	49.8	—	14	29	49.5	—

TABLE VII. (continued).

(c) *Solutions in N/18-Sodium Hydroxide.*

[illegible]

*One per cent. Solutions of Fructose and Glucose in Pyridine.*

In view of the interest attaching to the action of pyridine on the sugars, a few experiments were made with solutions of the two sugars in pure pyridine at 25°.

The pyridine was twice distilled over lime before use and boiled at 116–116·5°. Ten c.c. of the distilled pyridine caused no alteration in the blue tint of indigo or of methylene-blue (2 c.c. of the standard dye solutions) in twenty-four hours, but with 2 c.c. of *N*/100-permanganate a precipitate appeared in three hours.

The 1 per cent. fructose and glucose solutions in pyridine were also without action on the dyes, but results analogous to those of the weaker alkalis were obtained with permanganate. These are given in table VIII, in which the age of the solutions is in hours and the decolorisation times in minutes, as usual.

TABLE VIII.

*One per cent. Solutions of Fructose and of  $\alpha$ -Glucose in Pyridine.*

Age.	Fructose.		$\alpha$ -Glucose.			
0·1	30	not quite colourless	56	with very fine precipitation.		
1·0	23	" "	40	"	"	"
2·0	17	" "		"	"	"
3·5		" "	35	"	"	"
4·2	12	" "		"	"	"
5·0		" "	30	"	"	"
6·0	8	" "		"	"	"

*Comparative Experiments with Simple Aldehydes and Derivatives of Ethylene Oxide.*

Some experiments were made on the reducing action of aqueous solutions of acetaldehyde, *n*-butaldehyde, acetone, and epichlorohydrin and ethylene oxide. In neutral 1/18th gram-molecular solution all these substances, with the exception of acetone, caused the pink colour of the permanganate in our standard test to disappear within about two hours, but the resulting clear orange solution underwent no further change in colour for many hours. In the case of acetone, the pink tint did not entirely vanish for several hours.

The results of the permanganate tests in *N*/10-hydrochloric acid solution are given in the next table; in the case of ethylene oxide, the exact concentrations were not accurately known, but tests were made with two strengths, approximately gram-molecular per litre and 1/18th gram-molecular per litre.

TABLE IX.

*Solutions of Aldehydes and of Ethylene Oxides in  
N/10-Hydrochloric Acid.*

Substance.	Concn. per litre.	Age.	Permanganate tests.	
			Acid.	Neutralised.
Acetaldehyde ... M/18		0.1	6½ hrs. Pale yellow	9 minutes, with pptn.
		1.0	6½ hrs. " "	7 " "
		3.0	2 hrs. " "	10 " "
n-Butaldehyde ... M/18		0.1	3½ hrs. Pale yellow	13 minutes, with pptn.
		1.0	2½ hrs. " "	10 " "
		3.5	2½ hrs. " "	10 " "
		24.0	2½ hrs. " "	10 " "
Epichlorohydrin M/18		0.1	140 minutes.	82 minutes.
		1.5	120 "	53 "
		4.3	90 "	35 "
		24.0	120 "	32 "
Ethylene oxide ... M/18		0.1	103 minutes.	80 minutes.
		1.0	132 "	89 "
		3.0	130 "	80 "
		23.0	110 "	20 "
		M	0.1 8 minutes.	10 minutes.
			1.0 12 "	13 "
			2.0 17 "	14 "
			5.0 16 "	14 "
			23.0 15 "	14 "

Table X. illustrates the data obtained in N/18-aqueous sodium hydroxide; with both aldehydes, acetone, and epichlorohydrin and ethylene oxide, indigo passed rapidly through green to a pale yellow colour, and the original blue tint could not be restored by shaking the yellow solution with air. It appears, therefore, that some action was proceeding in these cases beyond simple reduction to indigo-white, and the colour test is not valid in this instance.

TABLE X.

*Solutions of Aldehydes and of Ethylene Oxides in N/18-Sodium Hydroxide.*

Substance.	Concn. per litre.	Age.	Methylene- blue.	Permanganate.	
				Alkaline.	Neutralised.
Acetaldehyde .....	M/18	0.1	60†	11*	11*
		1.0	32†	6*	50
		3.5	21†	16*	30
		5.0	23†	16*	18
		23.0	35†	6*	1

\* Precipitation set in.

† Indefinite end-point.



TABLE X. (continued).

*Solutions of Aldehydes and of Ethylene Oxides in N/18-Sodium Hydroxide.*

Substance.	Concn. per litre.	Age.	Methylene- blue.	Permanganate.	
				Alkaline.	Neutralised.
<i>n</i> -Butaldehyde.....	M/18	0.1	39†	8*	8*
		1.0	20	5*	8*
		3.5	14	7*	7*
		5.0	12	8*	8
		23.0	13	19*	2
Acetone.....	M/18	0.1	Permanent.	Pale green, then turbid yellow.	In 16 hours, precipitation, but still pink.
		1.3			
		3.3			
		5.3			
		23.0			
Epichlorohydrin .....	M/18	0.1	Permanent.	113*	207
		1.5	"	100*	140
		4.3	"	95*	116
		24.0	"	80*	110
Ethylene oxide .....	M/18	0.1	Permanent.	245†	352
		1.0	"	236†	350
		3.0	"	220†	340
		23.0	"	174†	320
	M	0.1	Permanent.	76†	87
		1.0	"	77†	84
		2.0	"	71	88
		5.0	"	55	77
		23.0	"	19*	53

\* Precipitation set in.

† Indefinite end-point.

The most interesting points in this series of experiments are:

(i) The alkaline solutions of the aldehydes reduce methylene-blue similarly to the sugars, and there is some similarity in their behaviour to alkaline permanganate.

(ii) The ethylene oxide derivatives show no similarity to the sugars in alkaline solution, either with respect to permanganate or to methylene-blue.

(iii) On the other hand, the acid solutions of the ethylene oxide compounds display great likeness to those of acid sugar solutions, both in the "acid" and "neutralised" permanganate tests.

WARRINGTON.

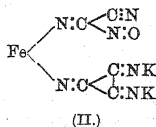
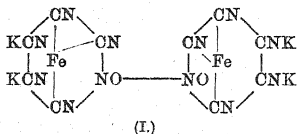
[Received, November 13th, 1919.]

CXXXIV.—*The Constitution of the Nitroprussides.*  
*Part I. Conductivity and Cryoscopic Measurements.*

By GEORGE JOSEPH BURROWS and EUSTACE EBENEZER TURNER.

From time to time, the nitroprussides have been made the subject of considerable speculation, but little attempt has been made to verify experimentally the various constitutions assigned to them.

Hofmann, who is responsible for most of the experimental work in this field (*Annalen*, 1900, **312**, 1), assigned to sodium nitroprusside the co-ordination formula  $[\text{Fe}(\text{CN})_5\text{NO}]\text{Na}_2$ . Friend (T., 1916, **109**, 721), apparently without further experimental work, proposed for potassium nitroprusside the formula (I).



This formula corresponds with the empirical one given in works of reference (for example, Moissan, "*Traité de chimie minérale*," 1905, 417), which formula, however, seems never to have had any evidence in its favour.

Friend at the same time rejected the formula (II) suggested by Browning (T., 1900, **77**, 1238) for potassium nitroprusside, in view of his theory as to the constitution of the ferrocyanides, which theory has since been shown to be unnecessary (Bennett, T., 1917, **111**, 490).

It was suggested by one of us (T., 1916, **109**, 1130) that a determination of the molecular weights of some nitroprussides would throw light on the problem, and, as a result, a number of nitroprussides have been prepared and investigated cryoscopically and their conductivities measured. From the results so obtained, the number of ions present in a solution of a nitroprusside has been calculated, and conclusions have been drawn as to the molecular weights of the salts in question. In these experiments, the degree of dissociation of the salt at any particular dilution was found in the usual way by dividing the molecular conductivity at that dilution by its value at infinite dilution. From cryoscopic measurements, the molecular depression of the freezing point of water was found for various concentrations of the salt, and by dividing this number by 18.7 (the molecular constant for water), the value for

$i$  (the van't Hoff coefficient) was obtained. The number of ions,  $k$ , into which each molecule of the salt dissociates was then obtained by substituting the experimental values of  $a$  and  $i$  in the equation

$$i = 1 + (k - 1)a.$$

A similar method was used by Petersen (*Zeitsch. physikal. Chem.*, 1902, **39**, 249) in connexion with the cobaltammines. This author was of the opinion that the conclusions drawn by Werner (*Zeitsch. physikal. Chem.*, 1893, **12**, 35, etc.) from measurements of the molecular conductivity at a dilution of 1000 litres (not necessarily at infinite dilution) were in most cases inaccurate.

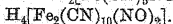
The figures given by Jones (*Carnegie Institute of Washington, Publication No. 170*) for the molecular conductivities of a large number of salts show that most salts are completely dissociated at dilutions of about 1000 litres. In some cases, however, the molecular conductivity again increases beyond that dilution, owing to causes other than dissociation. From the figures given by Petersen (*loc. cit.*) for the conductivity of the cobaltammines, it would appear that similar difficulties arose in his work.

In the present investigation, the substances considered are salts of a strong acid. (This has been found to be the case from a preliminary examination of the molecular conductivity of nitroprussic acid itself.) The conductivities of the salts were determined for solutions diluted to 2048 litres, and the values were plotted against the concentrations. The value for infinite dilution was found by extrapolation from the curve so obtained. In all cases, the value of  $\mu_{\infty}$  differs only slightly from the value actually found for  $\mu_{1024}$ , a result which was expected from the nature of the salts in question.

In the following tables are given the values of  $k$  calculated on the assumption that the nitroprussides are represented by the simple formula  $M_2[Fe(CN)_5NO]$ , which will be referred to in future as type I. In addition, the value of  $k_1$  has been calculated in each case for a molecule,  $M_4[Fe_2(CN)_{10}(NO)_2]$  (type II).

In the case of a univalent cation, a molecule of type I will dissociate into three ions, type II giving five ions. The value of  $k$  should therefore approximate to 3 if formula I is correct, whilst if II is correct,  $k_1 = 5$ . In the same way, a salt of a bivalent cation should give the values  $k = 2$  or  $k_1 = 3$ .

It is considered that the results obtained show conclusively that all the nitroprussides examined conform to the simple formula (type I). They are salts of  $H_2[Fe(CN)_5NO]$ , and not of



The possible effect due to hydration of the ions has not been overlooked (compare Jones, *Carnegie Institute of Washington, Publi-*

cation No. 180), and it is considered that the conclusions drawn from the figures obtained in the present work cannot be regarded as vitiated on this ground. Whereas hydrate formation may account for the differences between the experimental and absolute values of  $k$ , the extremely large differences in the case of  $k_1$  cannot be accounted for in this way.

It is hoped in a future communication to describe the alkyl nitroprussides, some of which have been prepared, although in an impure state only.

#### EXPERIMENTAL.

The conductivity measurements were all made at 25.0°. The degree of dissociation of salts at 0° differs only slightly from that at 25°, and the latter temperature allows of greater accuracy in determining the conductivity. In the following tables,  $v$  is the number of litres containing one gram-molecule of the salt (calculated for the simple formula I),  $\mu$  is the molecular conductivity,  $\alpha$  is the degree of dissociation and is equal to  $\mu/\mu_\infty$ ,  $\Delta_t$  is the observed depression of the freezing point of water,  $M\Delta_t$  is the molecular depression and is equal to  $v \times \Delta_t \times 10$ ,  $i$  is the van't Hoff coefficient and is equal to  $M\Delta_t/18.7$ , and  $k$  is the number of ions into which a molecule dissociates, and is obtained from the equation  $i = 1 + (k-1)\alpha$ ;  $k_1$  is the corresponding value of  $k$  calculated for a molecule of type II by doubling  $i$  and then substituting in the equation  $i = 1 + (k_1-1)\alpha$ .

The values of  $\alpha$  in the cryoscopic tables are taken from the curves obtained from conductivity data.

#### *Sodium Nitroprusside, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ .*

The salt used was a pure specimen.

#### *Conductivity Measurements.*

$v$ .	$\mu$ .	$\alpha$ .
4	155.2	0.63
8	169.4	0.69
16	181.8	0.74
32	194.3	0.79
64	204.9	0.84
128	214.2	0.87
256	222.0	0.91
512	229.2	0.94
1024	236.2	0.96
2048	244.6	—
$\infty$	245.0	—

*Cryoscopic Measurements.*

$v$	$\Delta_r$	$M\Delta_r$	$i$	$a = \mu_0/\mu_\infty$	$k$	$k_1$
47.1	0.115	54.1	2.90	0.81	3.35	6.9
24.4	0.218	53.2	2.84	0.77	3.40	7.1
14.55	0.345	50.2	2.68	0.73	3.30	7.0
10.81	0.456	49.3	2.64	0.71	3.30	7.0
8.76	0.560	49.1	2.62	0.70	3.31	7.0
7.12	0.678	48.3	2.58	0.68	3.32	7.1

Type I requires  $k=3$ . Type II requires  $k_1=5$ .

*Potassium Nitroprusside,  $K_2[Fe(CN)_5NO]$ .*

This salt was prepared by decomposing the barium salt with the calculated weight of pure potassium sulphate, filtering off the barium sulphate, and evaporating the filtrate at a low temperature under diminished pressure. The residue so obtained was crystallised from aqueous alcohol containing about 95 per cent. of alcohol. It crystallises in pale pink crystals without water of crystallisation:

0.4010 gave 0.1076  $Fe_2O_3$ .  $Fe=18.8$ .

$C_5ON_5FeK_2$  requires  $Fe=19.0$  per cent.

*Conductivity Measurements.*

$v$	$\mu$	$a$
8	199.2	0.745
16	205.2	0.795
32	215.7	0.836
64	227.2	0.881
128	236.6	0.917
256	244.0	0.946
512	249.3	0.966
1024	257.0	0.996
2048	258.1	—
$\infty$	258.0	—

*Cryoscopic Measurements.*

$v$	$\Delta_r$	$M\Delta_r$	$i$	$a = \mu_0/\mu_\infty$	$k$	$k_1$
34.4	0.150	51.6	2.76	0.85	3.07	6.32
24.1	0.213	51.3	2.74	0.82	3.12	6.46
14.66	0.316	46.3	2.48	0.79	2.87	6.01
11.65	0.405	47.2	2.52	0.77	3.00	6.25
7.02	0.641	45.0	2.41	0.74	2.91	6.16
4.78	0.909	43.4	2.32	0.71	2.86	6.11

Type I requires  $k=3$ . Type II requires  $k_1=5$ .

*Barium Nitroprusside,  $Ba[Fe(CN)_5NO] \cdot 3H_2O$ .*

This salt was prepared by precipitating a solution of the sodium salt with zinc sulphate and boiling the zinc salt so obtained with a suspension of precipitated barium carbonate. The filtered solution of the barium salt was evaporated under diminished pressure

at a low temperature, and the salt crystallised from aqueous alcohol:

0.8344 gave 0.4734  $\text{BaSO}_4$ .  $\text{Ba}=33.4$ .

$\text{C}_5\text{ON}_6\text{BaFe}_3\text{H}_2\text{O}$  requires  $\text{Ba}=33.7$  per cent.

The anhydrous salt was found to be extremely hygroscopic.

#### Conductivity Measurements.

$v$ .	$\mu$ .	$\alpha$ .
8	152.9	0.63
16	165.9	0.68
32	177.1	0.73
64	190.7	0.79
128	203.0	0.84
256	216.2	0.89
512	223.6	0.92
1024	236.9	0.98
2048	240.5	—
$\infty$	243.0	—

#### Cryoscopic Measurements.

$v$ .	$\Delta_t$ .	$M\Delta_t$ .	$i$ .	$\alpha=\mu_v/\mu_\infty$ .	$k$ .	$k_1$ .
37.7	0.093	35.1	1.88	0.74	2.19	4.73
16.5	0.180	29.7	1.59	0.68	1.87	4.21
9.87	0.285	28.1	1.50	0.64	1.78	4.13
6.67	0.413	27.6	1.47	0.61	1.77	4.18
4.73	0.575	27.2	1.45	0.59	1.76	4.22

Type I requires  $k=2$ . Type II requires  $k_1=3$ .

This salt is of especial interest, owing to the rough equality in weights of the anion and cation.

#### Ammonium Nitroprusside, $(\text{NH}_4)_2[\text{Fe}(\text{CN})_5\text{NO}]$ .

This salt was obtained by decomposing the barium salt with an equivalent weight of ammonium sulphate, filtering, evaporating under diminished pressure, and crystallising from aqueous alcohol, when reddish plates, very readily soluble in water, were obtained:

0.2390 gave 0.0768  $\text{Fe}_2\text{O}_3$ .  $\text{Fe}=22.5$ .

$\text{C}_5\text{ON}_6\text{Fe}(\text{NH}_4)_2$  requires  $\text{Fe}=22.2$  per cent.

#### Conductivity Measurements.

$v$ .	$\mu$ .	$\alpha$ .
16	206.7	0.77
32	218.0	0.82
64	228.5	0.85
128	236.7	0.89
256	245.6	0.92
512	251.2	0.94
1024	261.3	0.98
2048	266.2	—
$\infty$	268.0	—

*Cryoscopic Measurements.*

<i>v.</i>	$\Delta t.$	$M\Delta t.$	<i>i.</i>	$\alpha = \mu_v/\mu_{\infty}.$	<i>k.</i>	<i>k</i> <sub>1</sub> .
26.3	0.214	56.4	3.01	0.80	3.51	7.27
10.73	0.450	48.3	2.58	0.74	3.14	6.62
6.68	0.704	47.0	2.51	0.69	3.19	6.83

Type I requires  $k=3$ . Type II requires  $k_1=5$ .

*Methylammonium Nitroprusside, (MeNH<sub>3</sub>)<sub>2</sub>[Fe(CN)<sub>5</sub>NO].*

This salt and the nitroprussides of di- and tri-methylamine were obtained by treating a solution of the free acid (obtained from the barium salt and the calculated sulphuric acid) with a slight excess of an alcoholic solution of the amine. The solution so obtained was evaporated under diminished pressure, and the solid residue crystallised from alcohol. The alkylammonium nitroprussides crystallise in reddish plates, which are very readily soluble in water. In appearance they resemble the barium or ammonium salts:

0.1117 gave 0.0306 Fe<sub>2</sub>O<sub>3</sub>. Fe=19.2.

C<sub>5</sub>ON<sub>6</sub>Fe(MeNH<sub>3</sub>)<sub>2</sub> requires Fe=20.0 per cent.

*Conductivity Measurements.*

<i>v.</i>	$\mu.$	<i>a.</i>
32	185.2	0.77
64	197.7	0.82
128	208.0	0.87
256	218.5	0.91
512	225.8	0.94
1024	233.4	0.97
$\infty$	240.0	—

*Cryoscopic Measurements.*

<i>v.</i>	$\Delta t.$	$M\Delta t.$	<i>i.</i>	$\alpha = \mu_v/\mu_{\infty}.$	<i>k.</i>	<i>k</i> <sub>1</sub> .
36.6	0.148	54.2	2.90	0.78	3.45	7.2
19.05	0.262	49.9	2.67	0.71	3.35	7.1
14.15	0.339	48.0	2.57	0.68	3.31	7.1
10.13	0.466	47.2	2.52	0.62	3.45	7.5
8.35	0.541	45.2	2.42	0.59	3.41	7.5

Type I requires  $k=3$ . Type II requires  $k_1=5$ .

*Dimethylammonium Nitroprusside, (Me<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>[Fe(CN)<sub>5</sub>NO].*

0.1028 gave 0.0272 Fe<sub>2</sub>O<sub>3</sub>. Fe=18.5.

C<sub>5</sub>ON<sub>6</sub>Fe(Me<sub>2</sub>NH<sub>2</sub>)<sub>2</sub> requires Fe=18.1 per cent.

*Conductivity Measurements.*

<i>v.</i>	$\mu$ .	<i>a.</i>
16	156.5	0.68
32	172.1	0.75
64	185.2	0.81
128	196.3	0.85
256	205.8	0.90
512	212.5	0.92
1024	220.2	0.96
2048	227.3	—
	230.0	—

*Cryoscopic Measurements.*

<i>v.</i>	$\Delta t$ .	$M\Delta t$ .	<i>i.</i>	$a = \mu_v/\mu_\infty$ .	<i>k.</i>	$k_1$ .
35.2	0.149	52.4	2.80	0.76	3.37	7.05
16.4	0.294	48.1	2.57	0.68	3.31	7.09
8.84	0.500	44.2	2.36	0.61	3.23	7.10
5.92	0.714	42.3	2.26	0.57	3.21	7.20

Type I requires  $k=3$ . Type II requires  $k_1=5$ .

*Trimethylammonium Nitroprusside*,  $(\text{Me}_3\text{NH})_2[\text{Fe}(\text{CN})_5\text{NO}]$ .

0.2234 gave 0.0512  $\text{Fe}_2\text{O}_3$ .  $\text{Fe}=16.0$ .

$\text{C}_5\text{ON}_6\text{Fe}(\text{Me}_3\text{NH})_2$  requires  $\text{Fe}=16.7$  per cent.

*Conductivity Measurements.*

<i>v.</i>	$\mu$ .	<i>a.</i>
16	137.1	0.65
32	154.0	0.73
64	167.3	0.80
128	183.0	0.86
256	191.7	0.90
512	201.1	0.95
1024	208.0	0.98
2048	210.5	—
$\infty$	212.0	—

*Cryoscopic Measurements.*

<i>v.</i>	$\Delta t$ .	$M\Delta t$ .	<i>i.</i>	$a = \mu_v/\mu_\infty$ .	<i>k.</i>	$k_1$ .
39.0	0.134	52.2	2.79	0.75	3.39	7.11
14.47	0.290	42.0	2.24	0.63	2.97	6.52
6.56	0.588	38.6	2.06	0.50	3.12	7.24

Type I requires  $k=3$ . Type II requires  $k_1=5$ .

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CXXXV.—*The Propagation of Flame in Complex Gaseous Mixtures. Part I. Limit Mixtures and the Uniform Movement of Flame in such Mixtures.*

By WILLIAM PAYMAN.

IN order that flame may propagate through a mixture of an inflammable gas with air or oxygen, the heat developed by a given "layer" on burning must be sufficient to raise the contiguous layer of unburnt gas to its ignition temperature. In a "limit mixture" there is just sufficient, and only just sufficient, heat developed to accomplish this. If limit mixtures of two or more inflammable gases be mixed together, this heat balance should remain unaltered provided that all of the limit mixtures are of the same kind, that is to say, all lower-limit or all upper-limit mixtures. It follows that all mixtures, in any proportions, of limit mixtures should remain limit mixtures, the limiting percentage being that of the mixed inflammable gas. Conversely, any limit mixture of a complex inflammable gas will consist of a number of limit mixtures of the individual gases it contains.

Assuming this reasoning to be correct, imagine a limit mixture with air of a complex inflammable gas. Let  $A, B, C, \dots$  be the simple constituents of this inflammable gas, and their limits of inflammability,  $N_A, N_B, N_C, \dots$  respectively. Suppose also that the complex limit mixture contains  $a$  per cent. of  $A$ ,  $b$  per cent. of  $B$ ,  $c$  per cent. of  $C, \dots$ . Then this limit mixture will contain

$$aA + bB + cC + \dots + [100 - (a + b + c + \dots)] \text{air.}$$

This limit mixture, *ex hypothesi*, comprises a series of limit mixtures of the simple inflammable gases. In such a simple limit mixture of  $A$ , for example, every  $N_A$  parts of  $A$  are associated with  $100 - N_A$  parts of air, so that every  $a$  parts of  $A$  are associated with  $\left(\frac{100 - N_A}{N_A}\right)a$  parts of air. Similarly, for  $B, C, \dots$

The complex limit mixture will therefore contain

$$a + \left(\frac{100 - N_A}{N_A}\right)a, \quad b + \left(\frac{100 - N_B}{N_B}\right)b, \quad c + \left(\frac{100 - N_C}{N_C}\right)c, \dots$$

Since these terms are expressed as percentages, they will together equal 100, so that

$$a + \left(\frac{100 - N_A}{N_A}\right)a + b + \left(\frac{100 - N_B}{N_B}\right)b + c + \left(\frac{100 - N_C}{N_C}\right)c + \dots = 100.$$

This expression, on simplification, becomes

$$\frac{a}{N_a} + \frac{b}{N_b} + \frac{c}{N_c} + \dots = 1.$$

This is the formula of Le Chatelier, which has been shown to apply accurately for both the upper and lower limits of inflammability of a number of complex gaseous mixtures with air (Coward, Carpenter, and Payman, this vol., p. 27).

This "formula," but not the generalisation from which it has been deduced, applies only to mixtures of inflammable gases with an atmosphere of constant composition, such as air. For the numerical quantities involved in the formula relate to the combustible gases only, and admit of no allowance being made for variations in the proportions of inert gas present. The generalisation, however, should hold good for all limit mixtures; for mixtures in which the proportion of inert gas is greater or less than in air, or even in which its proportion is not constant.\*

The effect of an inert gas (nitrogen) on the limits of inflammability of methane has been investigated by Burgess and Wheeler (T., 1914, 105, 2596), who determined the limits for this gas in several artificial atmospheres of oxygen and nitrogen containing less oxygen than air. During the course of the present inquiry into the mode of combustion of mixed gases, it became necessary to extend their work to include atmospheres containing more oxygen than air, and pure oxygen.

The method of experiment used by Burgess and Wheeler, which involved the central ignition of the mixtures in a large globe, was not employed in the present research. This investigation is mainly concerned with the uniform movement of flame, and the determinations of the limits were made in the same apparatus as was used for measuring the speed of propagation of flame. This consisted of a horizontal glass tube 2.5 cm. in diameter, open at one end and closed at the other, the mixtures being ignited close to the open end of the tube by means of an electric spark. The criterion of inflammability was, therefore, the horizontal propagation of flame throughout the length of the tube.

The determinations were carried out by the method of trial and error, using mixtures which differed in composition by about 0.10 per cent. of methane. Throughout this paper, the term "limit mixture," whether upper or lower, implies that mixture in which flame was just able to propagate.

The results of the determinations are given in table I. The limits were always sharply defined. On sparking a mixture con-

\* This will be described in future as the "limits generalisation."

taining a little less than the lower-limit percentage of inflammable gas, there usually arose a ball of flame which travelled some 5 or 6 cm. along the tube. A mixture containing slightly more inflammable gas than the higher-limit percentage usually produced a flame which travelled the short distance from the spark to the open end of the tube, owing to the dilution of the mixture there by diffusion of the outside air. In the limit mixtures, flame travelled steadily and at an approximately uniform speed throughout the length of the tube.

In no instance did the flame of the burning limit mixture fill the whole cross-section of the tube, but it was usually similar to the trailing flames described by Burgess and Wheeler (T., 1914, 105, 2593). This was most marked with the upper-limit mixtures and with the lower-limit mixture of methane in pure oxygen. These flames were about 10 mm. in diameter and about 15 mm. long, and had a short tail, resembling a "Prince Rupert's drop" in shape.

In three instances the deposition of carbon was noticed during the passage of flame through a limit mixture, namely, in the upper-limit mixtures of methane with atmospheres containing 50, 66, and 100 per cent. of oxygen.\* The flames resembled that of a tallow candle, and the odour of the residual gases was similar to that caused by the smouldering wick of such a candle. In general, the upper-limit flames were olive-green in colour. The colour of the lower-limit flames was pale blue.

TABLE I.

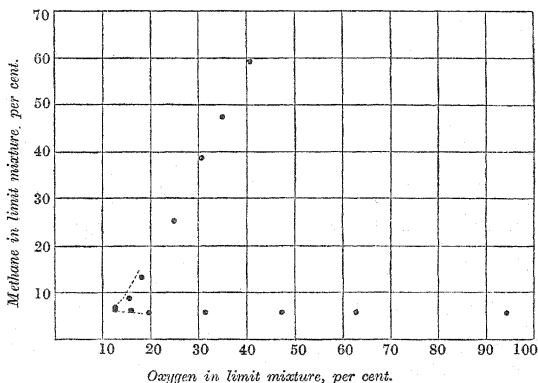
*The Limits of Inflammability of Methane in Mixtures of Oxygen and Nitrogen.*

Percentage of oxygen in atmosphere.	Percentage composition of limit mixtures.					
	Lower limit.			Upper limit.		
	CH <sub>4</sub> .	O <sub>2</sub> .	N <sub>2</sub> .	CH <sub>4</sub> .	O <sub>2</sub> .	N <sub>2</sub> .
13.7	6.4	12.8	80.8	6.9	12.7	80.4
17.0	6.1	16.0	77.9	8.9	15.5	75.6
21.0 (air)	5.8	19.8	74.4	13.3	18.2	68.5
33.0	5.8	31.4	62.8	25.1	25.0	49.9
50.0	5.8	47.1	47.1	38.8	30.6	30.6
66.0	5.8	62.8	31.4	47.5	35.0	17.5
100.0	5.7	94.2	—	59.2	40.8	—

\* According to Bone (*Phil. Trans.*, 1915, 215, 275), when methane and oxygen mixtures are exploded under pressure, "there is a total cessation of any separation of carbon (which is very marked with mixtures  $2\text{CH}_4 + \text{O}_2$ ) after the proportion of oxygen in the original mixture exceeds the limit  $3\text{CH}_4 + 2\text{O}_2$ ." No carbon was deposited when a mixture containing 59.3 per

The results are plotted in the diagram, the ordinates representing percentages of methane and the abscissæ percentages of oxygen in the limit mixtures.

If the "limits of generalisation" given earlier in this paper applies to these mixtures, the values for each of the two sets of limits should lie on a straight line. It will be seen that this holds accurately over a large range of mixtures, namely, over those containing more than about 17 per cent. of oxygen.\* Mixtures containing less than this amount of oxygen require rather more methane than the theoretical quantities to attain both the upper and lower limits.



The dotted lines in the diagram represent the values obtained by Burgess and Wheeler (*loc. cit.*). The shapes of both curves are cent. of methane and 40.7 per cent. of oxygen was exploded under a pressure of 12.7 atmospheres.

In the present series of experiments, at atmospheric pressure, a mixture of approximately the same composition as that used by Bone (59.2 per cent. of methane and 40.8 per cent. of oxygen) deposited carbon, as did also mixtures containing less oxygen in proportion to the methane present, namely, those intermediate in composition between  $3\text{CH}_4 + 2\text{O}_2$  and  $\text{CH}_4 + \text{O}_2$ . It would therefore appear that the limiting composition at which the deposition of carbon ceases is not fixed, but varies with the initial pressure of the mixture.

\* According to Burgess and Wheeler (*loc. cit.*), no mixture of methane, oxygen, and nitrogen is capable of propagating flame when there is less than about 13 per cent. of oxygen present.

similar, the difference in magnitude being due to the difference in experimental conditions.

Little change was observed in the lower limit until the mixtures contained a large excess of nitrogen; whilst the value with pure oxygen was only slightly lower than that with air. The latter observation is not in agreement with the results recorded by Parker (T., 1914, 105, 1002), who found the lower limit of inflammability of methane to be slightly higher with oxygen than with air (6.0 per cent. and 5.8 per cent. respectively). The apparatus used by Parker was similar to that previously used by Burgess and Wheeler, namely, a 2-litre globe in which the mixtures were ignited at the centre.

This lack of agreement is undoubtedly due to the difference in the position of the point of ignition in the two sets of experiments. It has frequently been noted that the limits of inflammability vary with the position of the point of ignition according as the flame has to pass upwards or downwards through the gas mixture. The fact that a flame will pass more readily upwards than downwards is well illustrated when a lower-limit mixture of methane in air, for example, is ignited by a spark at the centre of a globe. As soon as the spark passes, a flame shoots to the top of the vessel, bends over, and then moves slowly downwards to the bottom.

In order to investigate this point further, a series of experiments was carried out to determine quantitatively the effect of varying the point of ignition on the limits of inflammability of methane in air and in oxygen. A glass tube 2.5 cm. in diameter was used, closed at one end and fitted with firing points at the other (open) end.

TABLE II.

*Limits of Inflammability of Methane with Different Positions of the Point of Ignition.*

Mode of propagation.	Percentage of methane in lower-limit mixture.	
	Air.	Oxygen.
Upward .....	5.5	5.4
Horizontal .....	5.9	5.8
Downward .....	6.1	6.3
Central ignition (Parker)...	5.8	6.0

Both for upward and horizontal propagation the lower limit of inflammability of methane is less in oxygen than in air. For downward propagation, however, the order is reversed. The differences observed are not very great, although too large to be accounted for by experimental error. Of the factors which determine the value of the limiting percentage of inflammable gas, the

transference of heat by convection and the absorption of heat by the mixture may be mutually opposed. During the downward propagation of flame, convection does not materially affect the transference of heat to unburnt layers of the mixture; the influence of the slightly higher specific heat of oxygen as compared with that of nitrogen therefore becomes apparent. With horizontal and upward propagation of flame, however, the influence of convection currents masks the effect of the higher specific heat of oxygen.

The change of order of the results, dependent on the direction of travel of the flame, is more marked when the results for methane in air are compared with those for hydrogen. Such a comparison is made in table III.

TABLE III.

*Lower Limits of Inflammability in Air of Methane and of Hydrogen.*

Mode of propagation.	Percentage of inflammable gas	
	Methane.	Hydrogen.
Upward .....	5.5	4.2
Horizontal .....	5.9	6.2
Downward .....	6.1	9.7
Central ignition .....	5.8	9.2

Attempts have been made to calculate the limits of inflammability of a gas from its thermal constants. It will be clear from a consideration of the results recorded in table III that any such calculation is doomed to failure unless allowance can be made for the influence of convection currents.

Since the lower limit of inflammability of methane (downward propagation of flame) is less with air than with oxygen, it might be expected to be less still with an atmosphere containing less oxygen than air. This, however, is not so. The lower limit of inflammability of methane in an atmosphere containing 17 per cent. of oxygen was found to be 6.3 per cent. for downward propagation of flame. This limit is thus affected in the same sense as both limits for horizontal propagation in mixtures containing only a small percentage of oxygen; that is to say, more methane is required to form the limit mixture than would be expected from results with mixtures richer in oxygen.

This displacement of the range of inflammability corresponds with the displacement of the range for maximum speed of uniform movement of flame in mixtures of methane and air. It has been generally assumed that the latter displacement is due to the higher thermal conductivity of methane as compared with that of air. A

similar displacement is found, however, when the inflammable gas has a thermal conductivity less than that of air, as will be shown in a subsequent communication. The displacement under consideration in the present paper, and other similar displacements, have one feature in common, namely, that the mixtures contain a large proportion of inert gas (nitrogen), together with only a slight excess of one or other of the reacting gases above the quantity required for complete combustion.

A possible explanation of the results is that the mode of combustion in such mixtures differs from that in mixtures containing a large excess of either of the reacting gases. Such an explanation is supported by the analyses of the "flame gases" recorded by Burgess and Wheeler in the paper to which reference has already been made. The samples of gas were rapidly snatched from the flames in such a manner as to cool the primary products of combustion before secondary reactions could come into play. It will be seen on examining the table of analyses (p. 2604) that all mixtures containing less than 15 per cent. of oxygen appear to be influenced by the deficiency of reacting gas (whether methane or oxygen), and it is in these mixtures that the generalisation regarding limiting percentages no longer holds. With the upper-limit mixtures of low oxygen content, the primary products of combustion contain smaller quantities of hydrogen than of carbon monoxide, whereas with the higher-limit mixtures containing a greater proportion of oxygen, the quantities of hydrogen and carbon monoxide produced are equal.

Similarly with the lower-limit mixtures of low oxygen content, the primary products of combustion contain more carbon monoxide than hydrogen, whilst with lower-limit mixtures containing more than 15 per cent. of oxygen these gases are absent altogether from the products of combustion. Further consideration of these results is reserved for a future communication, as is also the consideration of the displacement of the range for maximum speed of uniform movement of flame in mixtures of air with inflammable gases.

#### *The Uniform Movement of Flame in Limit Mixtures.*

The speed of horizontal propagation of flame in the limit mixtures in a tube 2.5 cm. in diameter was determined by the method described by Wheeler (T., 1914, 105, 2606). The results are given in table IV.

TABLE IV.

*Speed of Propagation of Flame in Limit Mixtures of Methane, Oxygen, and Nitrogen in a Tube 2.5 cm. in Diameter.*

Percentage of oxygen in atmos- phere.	Speed in cm. per sec.	
	Lower limit.	Upper limit.
13.7	21.9	19.1
17.0	22.4	19.0
21.0 (air)	23.3	19.1
33.0	23.0	18.9
50.0	22.8	18.9
66.0	21.3	19.4
100.0	19.9	18.9

The upper-limit speeds are identical within the range of experimental error. The speeds in the lower-limit mixtures are throughout slightly higher than the corresponding upper-limit speeds, although with pure oxygen the difference is very small. A noticeable feature of these flames, common to them all, was their small size in comparison with the diameter of the tube. This was more marked with the flames in the upper-limit than in the lower-limit mixtures, a fact which no doubt accounts for the slower speed of the former flames. For the smaller the flame, the greater is its surface in proportion to its volume, and the greater in proportion is the transference of heat from the flame to the walls of the tube. If this explanation be correct, it follows that the speeds of flames in limit mixtures should increase with increased diameter of the tube in which they travel. This was found to be so by Mason and Wheeler (T., 1917, 111, 1052).

With tubes of very small diameter, on the other hand, the speed of flame at the limits is comparatively high (Payman and Wheeler, T., 1918, 113, 656), but for another reason. With such tubes, the cooling effect of the walls is so great as to have a marked effect on the value of the limits, the range of inflammability of the mixtures rapidly narrowing as the diameter of the tube is diminished. Moreover, convection currents have no appreciable influence in tubes of such small diameter.

It seemed probable that the speed of flame in a limit mixture, determined under standard conditions, should approach a constant value irrespective of the nature of the inflammable gas. To test this, the speeds of flame have been determined in limit mixtures of air with several of the paraffin hydrocarbons. The results are given in table V, which is of value also in recording the limits of inflammability (horizontal propagation of flame).

The limits differ slightly from those found (central ignition in



a large globe) by Burgess and Wheeler, whose results are inserted in the table in brackets.

In the upper-limit mixtures the flames vibrated rapidly about half-way along the tube, and were sometimes extinguished there. The difference between a limit mixture and one which could only propagate flame for a short distance, if at all, was, however, well marked.

TABLE V.

*Limits of Inflammability and Limiting Speeds of Flame in Mixtures of Air with the Paraffin Hydrocarbons in a Tube 2.5 cm. in Diameter.*

Hydrocarbon.	Lower limit.		Upper limit.	
	Per cent. of combustible.	Speed, cm. per sec.	Per cent. of combustible.	Speed, cm. per sec.
Methane, $\text{CH}_4$ .....	5.8 (5.6)	23.3	13.3 (14.8)	19.1
Ethane, $\text{C}_2\text{H}_6$ .....	3.3 (3.4)	18.1	10.6 (10.7)	19.7
Propane, $\text{C}_3\text{H}_8$ .....	2.4 (2.3)	20.8	7.3 ( 7.3)	20.3
Butane, $\text{C}_4\text{H}_{10}$ .....	1.9 (1.6)	20.1	6.5 ( 5.7)	20.3
Pentane, $\text{C}_5\text{H}_{12}$ .....	1.6 (1.4)	20.2	5.4 ( 4.5)	20.2
( $\text{CH}_4 + \text{C}_5\text{H}_{12}$ *) .....	2.6 (2.5)†	22.3	7.7 ( 7.7)†	20.7

\* Equimolecular mixture of methane and pentane.

† Calculated from values for methane and pentane.

The "limit speed" is thus found to approach a constant value, as foreshadowed by Burgess and Wheeler (T., 1914, 105, 2596), not only with each of the paraffin hydrocarbons singly, but also with the mixture of methane and pentane. There is no reason to doubt but that the limit speed of flame would have the same value for any mixture of the paraffins.

The speeds of flame in limit mixtures with air of carbon monoxide and hydrogen have also been determined. With carbon monoxide, the speed at both limits (in a tube 2.5 cm. in diameter) is 19.4 cm. per second, which agrees well with the speeds for the paraffins. With hydrogen, the speed at the lower limit is remarkably slow, namely, 10 cm. per second. The flame is exceedingly small, consisting of a tiny ball of flame, which, however, travels the full length of the tube. For reasons given in a previous communication (this vol., p. 41), it was not found possible to determine accurately the speed of flame in the upper-limit mixture of hydrogen and air.

The equimolecular mixture of methane and pentane corresponds with propane in percentage composition and calorific value, and yields the same products on complete combustion. The marked difference between the limits of inflammability of the mixed gases and those of propane shows that these are not the only factors on which the limits of inflammability depend. Similarly, a mixture

of three volumes of pentane and two volumes of hydrogen corresponds with propane, but this mixture of gases has limits 2.5 (lower) and 8.6 (upper) as compared with propane, 2.4 and 7.3.

These differences are perhaps due to the ability of the constituents of the mixed inflammable gases to burn independently. This subject will be dealt with more fully in succeeding papers of this series.

#### EXPERIMENTAL.

The speeds of propagation of flame in limit mixtures were determined in glass tubes by the method described by Wheeler (T., 1914, 105, 2610). Two tubes were employed, both 2.5 cm. in diameter; one, 3 metres long, used for the majority of the experiments; the other, used for the mixtures with atmospheres rich in oxygen, was only 1.5 metres long, so as to avoid the setting up of the detonation wave, with consequent shattering of the tube.

The platinum firing points were about 2 cm. from the open ends of the tubes. At measured distances along each tube were fused ground-glass tubulures, which carried glass plugs with stout platinum wires fused through them. Fine "screen wires" of copper were stretched across these platinum supports inside the tube, and electrical connexion was established with an automatic commutator and chronograph by means of platinum terminals on the outside of the plugs.

In order to fill the tubes with the mixture required for experiment, they were exhausted of air by means of an oil-pump, half filled with the mixture, and re-exhausted before being finally filled. A sample of the gas was then taken for analysis.

The limits of inflammability for upward and downward propagation of flame were determined in a similar tube 1.5 metres long, but without side-pieces.

The gases were prepared in the usual manner, the paraffin hydrocarbons being purified by repeated liquefaction and subsequent fractional distillation until, on explosion of a sample with excess of air and oxygen, the theoretical value for the ratio  $C/A$  was obtained.

The methane used in the limit determinations in pure oxygen contained 99.8 per cent. of  $\text{CH}_4$ , and the ratio  $C/A$  was found to be 2.00. The oxygen was prepared by gently heating recrystallised potassium permanganate, and contained 99.6 per cent. of  $\text{O}_2$ .

The gases were stored over water rendered alkaline by potassium hydroxide, and the mixtures were therefore saturated with water vapour.

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CXXXVI.—*The Propagation of Flame in Complex Gaseous Mixtures. Part II. The Uniform Movement of Flame in Mixtures of Air with the Paraffin Hydrocarbons.*

By WILLIAM PAYMAN.

In the preceding paper it was shown that all mixtures of limit mixtures are themselves limit mixtures. With each of the paraffin hydrocarbons, the speed of the uniform movement of flame at the limits tends to a constant value under standard conditions of experiment. The same speed was found with all limit mixtures of methane, oxygen and nitrogen, and with an equimolecular mixture of methane and pentane at its limits with air. There is no reason to doubt that the same speed would be obtained with all mixtures of the paraffin hydrocarbons at the limits.

The generalisation advanced in the previous paper was thus shown to apply to all such mixtures. The question immediately arises whether what is true of the speeds of flames at the limits holds also for other speeds. Whether, for example, given two or more mixtures of air with different individual gases, in each of which the speed of flame was the same, all combinations of the mixtures would propagate flame at the same speed. Should this be so, a simple method would be available for the calculation of the speed of propagation of flame in complex gaseous mixtures from the known values for the simple constituent gases. Such a calculation could naturally only apply over the whole range of mixtures when the maximum speed of flame in mixtures of the several individual gases with air was the same; otherwise calculation would be restricted to such mixtures as possessed a speed of flame not greater than the lowest of the individual maximum speeds. It is clear, also, that the mixtures taken for the purpose of calculation must be all of the same nature; that is to say, must all contain excess of combustible gas, or must all contain excess of oxygen.

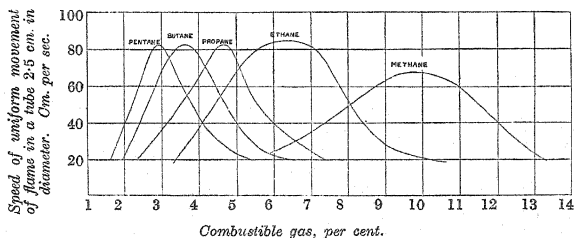
The mixtures of the paraffin hydrocarbons with air seemed most suitable to determine whether the generalisation that applies to speeds of flames at the limits is capable of extension to the speeds of the uniform movement over the whole range of inflammable mixtures.

Measurements were therefore made of the speed of the uniform movement in mixtures of air with each one of the hydrocarbons of the paraffin series up to and including pentane. The determinations were carried out as described in the previous paper, in a

horizontal glass tube 2.5 cm. in diameter and 3 metres long. The results are recorded in table I. The majority of the values in column 1 for methane were obtained by Mason and Wheeler (T., 1917, 111, 1052).

The results are shown diagrammatically in Fig. 1. With the exception of methane, the maximum speeds are approximately the same, namely, about 82 cm. per second. The value for methane is rather lower than this, being 67 cm. per second. Owing to the few data available for the thermal constants of the paraffin hydrocarbons, it is not easy to explain this difference. In each instance, the mixture having the maximum speed of flame contains more combustible gas than is required for complete combustion.

FIG. 1.



For testing the application of the generalisation\* to speeds other than the limiting speeds, the gases methane and pentane were first chosen, since they were both readily obtainable in ample quantity. Two air mixtures were prepared, one containing 7.35 per cent. of methane and the other 1.98 per cent. of pentane. In these two mixtures the speed of the uniform movement is the same, about 40 cm. per second (twice the speed at the limits), and they both contain excess of oxygen. The mixtures were then combined in varying proportions, and the speeds of the uniform movement determined in the usual manner. The results are recorded in table II.

\* This may be termed the "speed generalisation."



TABLE II.

*Speeds of Uniform Movement of Flame in a Glass Tube 2.5 cm. in Diameter with Mixtures containing 7.35 per cent. of Methane and 1.98 per cent. of Pentane, respectively, Mixed Together.*

Methane mixture. Per cent.	Pentane mixture. Per cent.	Speed, cm. per sec.
100.0	—	39.3
75.0	25.0	39.2
50.0	50.0	39.6
25.0	75.0	39.9
21.2	78.8	39.2*
—	100.0	40.1

\* Methane and pentane in equimolecular proportions.

It will be seen that the speeds are identical within the limits of experimental error.

Two mixtures containing excess of combustible gas, with speeds further removed from that at the limits, were then examined in the same manner. These mixtures contained 11.00 per cent. of methane and 3.54 per cent. of pentane, respectively, and the speed of the uniform movement of flame in them was about 60 cm. per second, three times the value at the limits. The results are given in table III.

TABLE III.

*Speeds of Uniform Movement of Flame in a Glass Tube 2.5 cm. in Diameter with Mixtures containing 11.00 per cent. of Methane and 3.54 per cent. of Pentane, respectively, Mixed Together.*

Methane mixture. Per cent.	Pentane mixture. Per cent.	Speed, cm. per sec.
100.0	—	59.1
75.0	25.0	59.1
50.0	50.0	60.3
25.0	75.0	59.1
24.4	75.6	59.1*
—	100.0	59.6

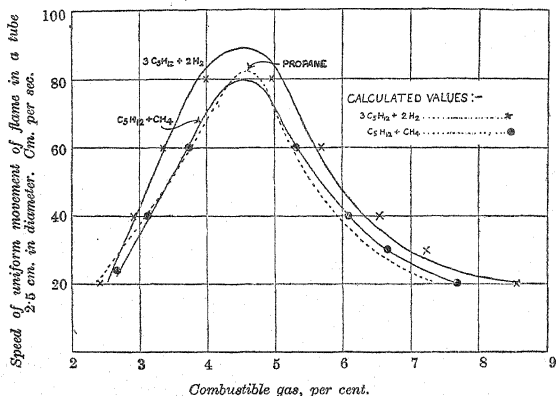
\* Methane and pentane in equimolecular proportions.

Once more the generalisation is found to hold with great accuracy, and there is no doubt that it is true for all mixtures of the paraffins having the same speeds of flame provided that the maximum speed in mixtures of any individual paraffin with air is not too nearly approached. For if the generalisation could be supposed to apply to the "maximum-speed" mixtures, no mixture of air containing both methane and pentane should propagate the

uniform movement of flame at a speed higher than the maximum speed in mixtures of methane and air. Similarly, the generalisation cannot apply to speeds at the limits in mixtures of methane with atmospheres containing a high proportion of nitrogen, for with such atmospheres both upper and lower limits of inflammability lie at the maximum, flattened portion of the speed-percentage curve.

Bearing these limitations in mind, it should be possible to calculate the values for the speed-percentage curve for any combination of the paraffins in air. An equimolecular mixture of methane and

FIG. 2.



pentane (which corresponds with propane) was chosen to test the accuracy of such calculations.

The results are recorded in table IV, and are compared with the calculated values in Fig. 2. In no instance was the difference between observed and calculated speeds greater than 1 cm. per second. The highest speed for which calculation was made was 60 cm. per second.

It must be admitted that the gases chosen for these experiments are particularly favourable towards the calculation, since the maximum speed of the uniform movement is nearly the same with each gas. As a more stringent test, a mixture of pentane and hydrogen was prepared ( $3C_5H_{12} + 2H_2$ , corresponding with propane), and a

series of speed determinations and calculations made as before. In this instance, the maximum speeds of uniform movement in mixtures of the individual gases with air differ widely, being 82 cm. per second for pentane and 485 cm. per second for hydrogen. The results are recorded in table IV, and in Fig. 2 are compared with those calculated.

TABLE IV.

*Speed of Uniform Movement of Flame in Mixtures of Air with Combinations of Gases corresponding with Propane in a Glass Tube 2.5 cm. in Diameter.*

(a) $\text{CH}_4 + \text{C}_5\text{H}_{12}$ .		(b) $3\text{C}_5\text{H}_{12} + 2\text{H}_2$ .	
Combustible gas. Per cent.	Speed, cm. per sec.	Combustible gas. Per cent.	Speed, cm. per sec.
2.55	6 cm. travel only	2.35	Cap only
2.65	22.3	2.47	19.7
3.12	39.2	3.02	43.3
3.54	53.7	3.56	67.7
4.04	70.7	4.03	82.7
4.52	78.3	4.48	89.5
5.05	73.6	4.91	83.7
5.36	59.1	5.77	54.0
6.23	37.5	6.25	43.6
7.03	25.4	7.10	27.9
7.70	20.7	7.80	23.1
7.79	3 cm. travel only	8.60	21.5
		8.72	15 cm. travel

The results are not in as good agreement with calculation as those obtained with the combination of methane and pentane, but, even so, the agreement is remarkably close considering the wide difference between the individual maximum speeds of flames. The greatest difference between observed and calculated results is only 4 cm. per second. The highest speed for which calculation was made was 60 cm. per second, which is rather close to the maximum speed for pentane.

It will no doubt be apparent that a limit is at present set to the scope of the generalisation, because only the speeds of flames in mixtures with air are available for purposes of calculation. When it is remembered that the gas with the slower maximum speed of uniform movement of flame may have that maximum greatly enhanced if an atmosphere richer in oxygen than air is used, it is clear that the generalisation should be capable of further extension, given the necessary experimental data. The consideration of this subject is reserved for a later paper.

It now remains to deduce a method for calculating the maximum speed of the uniform movement of flame in a mixture of air with a mixture of inflammable gases, and also for calculating the com-



position of the mixture which will have this maximum speed of flame. The latter may be calculated by the method suggested in a previous communication (Payman and Wheeler, this vol., p. 36), in which it was shown that if "maximum-speed" mixtures were mixed together, the result would be the "maximum-speed" mixture for the mixed inflammable gases. For example, the value for the maximum speed of uniform movement of flame for hydrogen is 38.5 per cent., for pentane 2.9 per cent., and for methane 9.9 per cent.\* The calculated value for the equimolecular methane-pentane mixture is 4.48 per cent., and for the pentane-hydrogen mixture ( $3C_5H_{12} + 2H_2$ ) 4.60 per cent. The value found is the same for both mixtures, namely, 4.55 per cent. It is interesting to note that the same value is found for propane, with which these mixed inflammable gases correspond.

It was also suggested, from a consideration of the results obtained with mixtures of air with an equimolecular mixture of methane and hydrogen, that the gas for which the maximum speed of flame was the lower had the predominating effect in determining what would be the maximum speed with mixed inflammable gases. This is true for mixtures of methane and hydrogen, but, in general, it is the gas requiring most air to attain the maximum speed of flame which is the deciding factor. This is, indeed, what one would expect from a consideration of the generalisation concerning the speeds in mixed gases. The larger the volume of air a combustible gas requires to produce its "maximum-speed mixture," the smaller is the percentage of that combustible gas in the fastest-speed mixture of air with a mixture of gases that contain it.

A method for calculating approximately the maximum speed of the uniform movement of flame in mixtures of air with a mixed inflammable gas, from the known values for its simple constituents, may be given from a consideration of this fact. The assumption is made that when "maximum-speed" mixtures are mixed together, the resulting speed is proportional to the amount of each mixture present and to the respective maximum speeds of their flames. This relationship, which holds roughly for mixtures with air, may be expressed as follows:

$$S = \frac{aS_a + bS_b + cS_c + \dots}{a + b + c + \dots};$$

where  $S$  is the speed required;  $a, b, c, \dots$  are the amounts present of each maximum-speed mixture with air;  $S_a, S_b, S_c, \dots$  are the speeds of flame in those mixtures respectively.

The use of the formula will be best explained by an actual

\* In each instance the figure given is the mean percentage over a range of mixtures having nearly the same speed.

calculation of the maximum speed of flame for the equimolecular mixture of methane and pentane in admixture with air.

The calculated value for the mixture to have the maximum speed of flame is 4.5 per cent., and this mixture will contain 2.25 per cent. each of methane and pentane. In the maximum-speed mixture of pentane and air, 100 parts of the mixture contain 2.9 parts of pentane, and therefore 2.25 parts of pentane correspond with  $\frac{2.25}{2.9} \times 100 = 77$  parts of pentane-air mixture.

Similarly, 2.25 parts of methane correspond with 23 parts of methane-air mixture, since the maximum-speed mixture of methane and air contains 9.9 per cent. of methane.

Substituting these values in the above formula,

$$S = \frac{(77 \times 82) + (23 \times 67)}{100} \\ = 78.5 \text{ cm. per second.}$$

The value found was 79 cm. per second, showing an extremely close agreement.

The agreement is not so good with the pentane-hydrogen mixture ( $3\text{C}_5\text{H}_{12} + 2\text{H}_2$ ), the calculated value being 100 cm. per second and the speed found 90 cm. per second. The discrepancy does not appear so great, however, when it is remembered that there is a difference of 400 cm. per second between the maximum speeds of the flames in mixtures of pentane and air and hydrogen and air.

The maximum speed of flame with mixed gases and air may also be found by a graphical method. If on a speed-percentage graph the maxima for any two gases taken singly is joined by a straight line, all the maxima for mixtures of these two gases lie approximately on this line. The composition of the "maximum-speed" mixture is calculated by the method given by Payman and Wheeler (*loc. cit.*), and the speed then read off from the graph.

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CXXXVII.—*The Propagation of Flame in Complex Gaseous Mixtures. Part III. The Uniform Movement of Flame in Mixtures of Air with Mixtures of Methane, Hydrogen and Carbon Monoxide, and with Industrial Inflammable Gases.*

By WILLIAM PAYMAN.

THE common industrial gases contain as their inflammable constituents methane, hydrogen, and carbon monoxide in various proportions.

The speed of the uniform movement of flame in mixtures of methane and air in a tube 2.5 cm. in diameter was given in Part II of this series of papers. The speeds with hydrogen and air in a similar tube (over the major portion of the range of inflammable mixtures) have been determined by Haward and Otagawa (T., 1916, 109, 83). The speeds in mixtures of carbon monoxide and air are recorded in the present paper.

*Mixtures of Carbon Monoxide and Air.*—It is well known that the rate of combustion of carbon monoxide is dependent on the amount of water vapour present. Dixon, for example (*Phil. Trans.*, 1893, 184, 97), has shown that the velocity of the detonation wave in a mixture of carbon monoxide and oxygen ( $2\text{CO} + \text{O}_2$ ) increases with the percentage saturation of water vapour.

The present series of determinations of the speed of the uniform movement of flame in mixtures of carbon monoxide and air was carried out with mixtures saturated with water vapour at the ordinary temperature and pressure. Since the room temperature varied, it was not surprising to find that the speed in a given mixture did not remain constant from day to day. Identical results were, however, obtained in experiments made within a few minutes of each other at the same temperature and pressure. Table I illustrates the effect of change in the percentage saturation of water vapour on the speed of the uniform movement of flame in a mixture of carbon monoxide and air containing 50 per cent. of carbon monoxide.

TABLE I.

*Speed of Uniform Movement of Flame in a Mixture of Carbon Monoxide and Air (50 per cent. CO) in a Tube 2.5 cm. in Diameter.*

Temperature and pressure.	Cm. per sec.	
10° and 750 mm. ....	(1) 59.9	(2) 59.9
15° and 750 mm. ....	(1) 65.0	(2) 64.5
17° and 755 mm. ....	(1) 79.4	(2) 79.0

A series of determinations of speeds of flame over the whole range of inflammable mixtures was carried out during a period when the temperature of the laboratory did not alter appreciably (about 12°). The values obtained are given in table II.

TABLE II.

*Speed of Uniform Movement of Flame in Mixtures of Carbon Monoxide and Air in a Tube 2.5 cm. in Diameter at 12° and 750 mm.*

Per cent. of carbon monoxide.	Cm. per sec.	Per cent. of carbon monoxide.	Cm. per sec.
16-15	Tongue of flame only.	59.81	54.2
16-29	19.5	65.55	37.4
16-40	19.4	65.84	36.3
16-51	19.4	67.10	30.2
24.47	34.0	67.57	29.6
30.50	46.0	69.00	26.0
44.84	60.1	70.63	20.0
50.45	59.9	70.68	20.3
54.40	57.8	71.19	19.4
59.58	56.2	71.31	Trailing flame travelled 15 cm.

These values are of interest in themselves, apart from their connexion with the problem of the propagation of flame in complex gaseous mixtures, inasmuch as they disclose the fact that the maximum speed of flame is obtained with mixtures containing from 45 to 50 per cent. of carbon monoxide. The mixture for complete combustion contains 29.5 per cent. carbon monoxide, so that the "displacement" of the maximum-speed mixture is greater even than with hydrogen, despite the fact that the thermal conductivity of carbon monoxide is but little different from that of air.

Industrial gas mixtures may contain varying proportions of water vapour. There may therefore be some uncertainty as to the correct values to use for the speed of flame in mixtures of carbon monoxide and air when attempting to calculate the speed of flame in the mixed industrial gas. Such gases, however, contain hydrogen as well as carbon monoxide, and the presence of hydrogen affects the speed of flame in a similar degree to that of water vapour. With mixtures of gases containing fairly high proportions of hydrogen, it is therefore not unlikely that the effect of variation in the moisture content would be inappreciable. It should therefore be sufficient for our purpose to know the values for the speed of flame in mixtures of air with a mixture of hydrogen and carbon monoxide. Or the "effective" speeds for mixtures of carbon monoxide and air could be calculated from such values and these speeds used for further calculation.

In this connexion, it is interesting to note that Berthelot (*Ann. Chim. Phys.*, 1881, [v], 28, 289) found the rate of detonation in mixtures of carbon monoxide and oxygen to be about half the calculated value. For mixtures of oxygen with carbon monoxide plus hydrogen, the calculated values were in good agreement with those found. Similarly, in the present research, the maximum speed of uniform movement of flame in mixtures of carbon monoxide and air is found to be about half the value calculated, making use of the values determined for hydrogen-air and hydrogen-carbon monoxide-air mixtures.

*Mixtures of Hydrogen and Air.*—As with tubes of smaller diameter (this vol., p. 36), it was not found possible to determine accurately the speed of the uniform movement of flame in the upper-limit mixture of hydrogen and air in a tube 2.5 cm. in diameter. A mixture containing 71.4 per cent. of hydrogen was found to be the richest which would propagate flame under the experimental conditions. The flame was not hot enough to melt "screen wires," but its speed, as measured by means of a tapping key in connexion with a chronograph, was found to be approximately 50 cm. per second.

A characteristic of the lower-limit mixture and of mixtures near to it is the formation on ignition of minute balls of flame, which pass steadily from the open to the closed end of the tube. These flames are propagated mainly by the influence of convection currents, and the speed-percentage curve at the lower-limit region is not continuous, but shows a definite break. Nevertheless, no definite distinction, at the point of break in the curve, could be drawn between the normal and the balls of flame, the latter increasing in size and gradually changing their form as the percentage of hydrogen increased.

The speeds of the flames in mixtures near the limits are given in table III, which completes the table given by Haward and

TABLE III.

*Speed of the Uniform Movement of Flame in Mixtures of Hydrogen and Air in a Tube 2.5 cm. in Diameter.*

Hydrogen. Per cent.	Speed, cm. per sec.
8-10	No flame observed.
6-19	10
6-31	12
6-52	15
14-71	120
71-39	50
71-51	Flame to open end only.

Otagawa (*loc. cit.*, p. 89). In only one instance was the flame hot enough to melt "screen wires," namely, with the mixture containing 14.71 per cent. of hydrogen; the remaining speeds were determined by means of a tapping key.

*Mixtures of Methane, Hydrogen, and Air.*—The speed of the uniform movement of flame in a tube 2.5 cm. in diameter was determined over a range of mixtures of air with two mixtures of methane and hydrogen. The first mixture contained equal volumes of methane and hydrogen ( $\text{CH}_4 + \text{H}_2$ ), the second three volumes of methane to one volume of hydrogen ( $3\text{CH}_4 + \text{H}_2$ ). The results are recorded in table IV. The lower-limit flames preserved the general character of the corresponding hydrogen flames, and their speeds were found to be lower than the speed in the limit mixture of methane and air.

TABLE IV.

*Speed of the Uniform Movement of Flame in Mixtures of Air with Hydrogen Methane Mixtures in a Tube 2.5 cm. in Diameter.*

$\text{CH}_4 + \text{H}_2$ .		$3\text{CH}_4 + \text{H}_2$ .	
Combustible gas.	Speed,	Combustible gas.	Speed,
Per cent.	cm. per sec.	Per cent.	cm. per sec.
6.03	15.0	6.09	18.0
6.20	17.1	6.22	19.9
6.31	19.1	6.50	21.0
6.73	22.1	6.80	27.7
7.68	28.6	7.84	39.6
9.05	45.6	9.06	58.3
10.23	67.4	9.93	78.7
11.95	104.1	11.35	84.9
11.99	106.3	12.26	82.2
13.50	128.6	13.25	66.7
14.93	135.3	14.20	45.7
15.93	127.3	14.99	27.8
16.90	111.9	15.50	22.6
18.31	65.6		
19.96	35.5		
20.22	30.5		
20.32	28.5		
20.48	27.3		
20.80	24.3		

The results are plotted as curves in Fig. 1, the calculated curves being shown in dotted line. The maximum speeds calculated by the method given in Part II are 150 and 99 cm. per second respectively for the mixtures  $\text{CH}_4 + \text{H}_2$  and  $3\text{CH}_4 + \text{H}_2$ . The values found were 135 and 85 cm. per second.

*Mixtures of Carbon Monoxide, Hydrogen, and Air.*—Two mixtures of carbon monoxide and hydrogen were employed, of composition  $\text{CO} + \text{H}_2$  and  $3\text{CO} + \text{H}_2$ , corresponding with the methane-hydrogen mixtures. The results are given in table V, and are plotted as curves in Fig. 2.

FIG. 1.

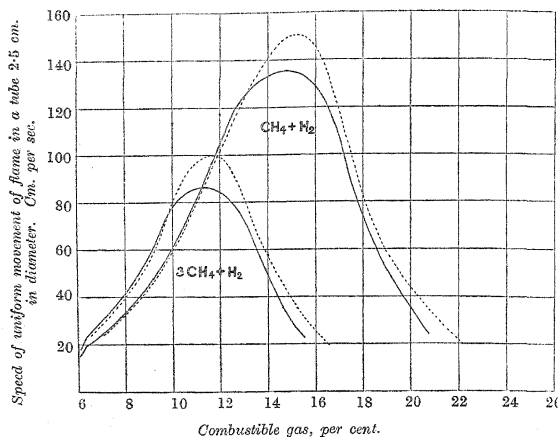
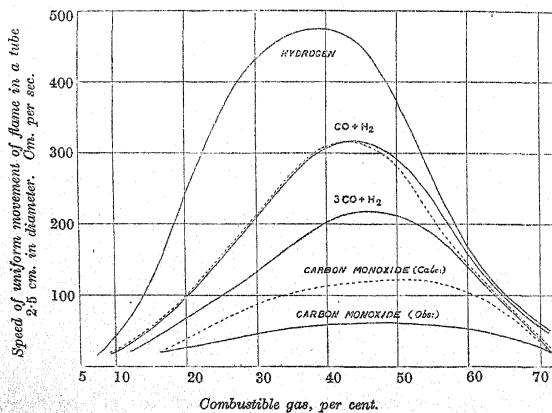


FIG. 2.



From the values found for hydrogen and for the mixture  $3\text{CO} + \text{H}_2$ , the speeds of the flames in mixtures of air with  $\text{CO} + \text{H}_2$  were calculated. The results are shown in dotted line in Fig. 2. The values for carbon monoxide and air were also calculated from these values, and the curve is given in the diagram for comparison. It will be seen that the values calculated in this manner are much higher than those found by experiment. These "effective" speeds have been used in subsequent calculations instead of the values as determined, which are dependent on the amount of water vapour present.

TABLE V.

*Speed of Uniform Movement of Flame in Mixtures of Air with the Mixtures  $\text{CO} + \text{H}_2$  and  $3\text{CO} + \text{H}_2$  in a Tube 2.5 cm. in Diameter.*

$\text{CO} + \text{H}_2$ .		$3\text{CO} + \text{H}_2$ .	
Combustible gas. Per cent.	Speed, cm. per sec.	Combustible gas. Per cent.	Speed, cm. per sec.
9.25	18.2	12.00	19.2
10.35	21.1	18.99	67.1
15.40	58.3	27.82	115.0
20.57	100.4	34.73	166.2
30.25	211.5	41.32	205.5
36.94	282.9	46.90	214.0
41.50	309.7	53.17	200.0
45.92	315.2	58.49	154.7
51.23	280.0	70.36	34.4
58.55	178.5	71.42	20.8
69.00	64.5		
70.75	50.1		
71.34	44.4		

*Mixtures of Methane and Carbon Monoxide, and Mixtures of Methane, Hydrogen, and Carbon Monoxide with Air.*—Table VI records the results obtained with a mixture containing equal volumes of methane and carbon monoxide, and with one containing equal volumes of methane, hydrogen, and carbon monoxide. Methane, or any gas into the composition of which hydrogen enters, acts towards mixtures of carbon monoxide and air in a manner comparable with that of hydrogen and water vapour. The maximum speed of uniform movement of flame in mixtures of air with each of the mixtures  $\text{CH}_4 + \text{CO}$  and  $\text{CH}_4 + \text{CO} + \text{H}_2$  was found to be 91 and 150 cm. per second respectively, whilst the corresponding calculated values are 78 and 145 cm. per second.

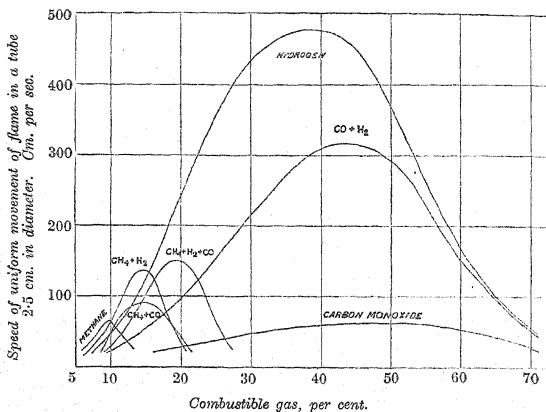


TABLE VI.

*Speed of Uniform Movement of Flame in Mixtures of Air with the Mixtures  $\text{CH}_4 + \text{CO}$  and  $\text{CH}_4 + \text{H}_2 + \text{CO}$  in a Tube 2.5 cm. in Diameter.*

$\text{CH}_4 + \text{CO}$ .		$\text{CH}_4 + \text{H}_2 + \text{CO}$ .	
Combustible gas.	Speed,	Combustible gas.	Speed,
Per cent.	cm. per sec.	Per cent.	cm. per sec.
9.45	21.9	7.70	21.2
9.88	36.2	10.01	36.5
12.07	62.5	14.01	83.3
13.73	85.7	15.80	109.4
15.95	91.3	18.92	150.0
18.06	68.9	20.42	148.7
19.32	52.3	22.43	118.5
21.55	19.8	25.05	57.8
		27.57	21.8

FIG. 3.



The speed-percentage curves for the equimolecular mixtures  $\text{CH}_4 + \text{H}_2$ ,  $\text{H}_2 + \text{CO}$ ,  $\text{CO} + \text{CH}_4$ , and  $\text{CH}_4 + \text{H}_2 + \text{CO}$  are plotted in Fig. 3, the curves for the pure gases being included for comparison.

*Mixtures of Industrial Gases with Air.*—The equimolecular mixture of carbon monoxide and hydrogen correspond nearly with "water-gas." A coal-gas and a producer-gas were also examined, the compositions of these being:

	Coal-gas. Per cent.	Producer-gas. Per cent.
Benzene and higher olefines .....	1.1	—
Carbon dioxide .....	0.3	5.0
Ethylene .....	2.6	—
Carbon monoxide .....	9.6	21.3
Hydrogen .....	49.2	12.6
Methane and higher paraffins .....	33.9	3.1
Nitrogen (by difference) .....	3.3	58.0

The speeds of the uniform movement of flame in mixtures of air with each of these two gases are given in table VII.

TABLE VII.

*Speed of Uniform Movement of Flame in Mixtures of Air with Coal-gas and with Producer-gas in a Tube 2.5 cm. in Diameter.*

Coal-gas. Per cent.	Speed, cm. per sec.	Producer-gas. Per cent.	Speed, cm. per sec.
7.2	21.5	24.7	20.0
10.0	50.5	38.9	47.4
11.9	87.1	46.0	62.7
14.7	133.7	49.0	72.2
16.8	153.9	54.3	69.7
17.9	154.1	58.8	43.5
20.4	115.6	61.6	24.0
21.8	74.3		
24.3	22.0		

The principal constituents of the coal-gas are hydrogen, methane, and carbon monoxide. If all the hydrocarbons be reckoned as methane, the calculated maximum speed of uniform movement of flame in mixtures of air with this coal-gas is 164 cm. per second, with a mixture containing 18.4 per cent. of coal-gas. Since the content of inert gases (nitrogen and carbon dioxide) is low, they may be neglected when making the calculations.

Producer-gas, on the other hand, always contains a large proportion of inert gas; the sample used for these experiments contained only 37 per cent. of combustible gas. For this reason, a value for the maximum speed of uniform movement of flame in a mixture of producer-gas and air, calculated from the maximum speeds in mixtures of the pure gases with air, would be too high.

The speed of flame in mixtures of air with gas containing a large proportion of nitrogen can be calculated on the assumption that the cooling or retarding effect on the flame of excess of air or of nitrogen will be the same, since their specific heats are the same.\* A mixture of carbon monoxide, hydrogen, and methane in the pro-

\* This assumption is not quite correct, since the presence of reactive gas slightly opposes the retarding effect of air.

portions in which they are found in the sample of producer-gas used in these experiments will have as its "fastest-speed" mixture with air one containing 34.7 per cent. of combustible gases. If nitrogen is added to this mixture, so that the ratio of nitrogen to combustible gases is the same as in the producer-gas, the result is a mixture containing 21.7 per cent. of combustible gases. (The carbon dioxide content being low, it may be calculated as nitrogen.) The speed of flame in this mixture should, on the assumption given above, be but little different from the speed of flame in the same mixture of combustible gases with air. The latter speed is most easily determined by a graphical method, and is found to be 85 cm. per second.

The mixture of air and producer-gas with the fastest speed of uniform movement of flame contains slightly more inflammable gases than is required for complete combustion. A greater "displacement" of the maximum-speed mixture might be expected for the reason that the chief inflammable constituents are hydrogen and carbon monoxide, the individual displacements of which are considerable. The small displacement with producer-gas is due to the presence of inert gases, as will be explained in the succeeding section of this series of researches. The effect, in general, of inert gases on the speed of the uniform movement of flame in gaseous mixtures will also be considered.

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### CXXXVIII.—*The Ignition of Ether-Alcohol-Air and Acetone-Air Mixtures in Contact with Heated Surfaces.*

By ALBERT GREVILLE WHITE and TUDOR WILLIAMS PRICE.

OWING to the large number of fires which had occurred during 1917 and 1918 in solvent-recovery stoves in which cordite was being dried, it was decided to investigate the conditions under which mixtures of the vapours of ether, alcohol, and acetone with air would ignite. This was rendered all the more necessary by the fact that the information available on this subject was scanty and often contradictory.

As a general rule, the actual rise in temperature necessary to cause the explosion of such an explosive as glyceryl trinitrate is much lower than that needed to ignite an explosive gaseous mix-

ture. On the other hand, the lower thermal capacity of the gas and its comparatively far greater mobility render it more susceptible to ignition in many cases. There was thus some justification for the idea that the solvent-air mixture was probably responsible for many of the recovery-stove fires that had occurred, particularly when it is remembered that fires had been less frequent in "final" stoves than in recovery-stoves, that more fires had occurred with cordite from which a mixture of ether and alcohol was being removed than when the solvent was acetone, and that ether when mixed with air is indubitably more dangerous than acetone under similar conditions.

The factors affecting the ignition of a combustible gaseous mixture are many, and the influence of some of them is not particularly well understood. The problem of safety when dealing with such a mixture under manufacturing conditions divides itself naturally into two parts, the one dealing with the ignition of the mixture, and the other with the propagation of the flame from one portion of the mixture to another, for example, from one building to another. This division is seen to be inherent when it is remembered that, by using a sufficiently powerful source of ignition, it is possible to ignite almost any combustible gas-air mixture, whereas the propagation of the flame is a totally different matter, particularly if the gas-mixture considered is at rest. In such a case, there appear to be definite limits for the proportion of combustible gas to air in a mixture which propagates flame, these limits depending ultimately only on the direction of propagation and the nature of the combustible gas used, at ordinary temperature and pressure. The experimental work is accordingly divided into three sections:

- (1) The ignition-temperatures of various gas-mixtures, including ether-air, alcohol-air, and acetone-air mixtures.
- (2) The limits for the propagation of flame in these mixtures.
- (3) The investigation of a few miscellaneous facts concerned more particularly with various means of ignition.

The fact has not been lost sight of that ease of ignition and propagation of flame might be enhanced by the presence of some impurity in the solvent vapour-air mixture. Accordingly, experiments have been carried out to ascertain the effect of adding slight amounts of glyceryl trinitrate and of the peroxides of ether to the gas-mixtures dealt with. This was the more necessary, as glyceryl trinitrate, even though present in the stove vapours in minute quantities, is known to be a source of possible danger, and also because there appears to be a tendency to assign any otherwise inexplicable explosion or fire with ether to the influence of these

peroxides (compare Neander, *Chem. Zeit.*, 1902, **26**, 336, and others). This idea seems to have arisen chiefly from the fact that ether which had given trouble had generally been kept for some time, and also because it was well known that the exposure of purified ether to light caused the formation of compounds which appeared to contain active oxygen. The methods used to prepare these compounds were those given by Baeyer and Villiger (*Ber.*, 1900, **33**, 3387; 1901, **34**, 738). Naturally, great care was exercised in freeing the solvents used from such impurities.

The ether used was twice distilled from acid permanganate and washed several times, first with a concentrated solution of potassium hydroxide in water, and then with a dilute one. It was then washed several times with distilled water, dried, distilled, and again dried for several days over sodium. On fractionating twice with a Young and Thomas still-head, a fraction boiling within  $0.05^{\circ}$  of the boiling point of the pure substance was collected each time. The alcohol used was ordinary absolute alcohol, which was twice heated under reflux for four hours over fresh lime, then twice over calcium turnings for two hours, and refractionated as for ether, the fraction collected boiling within  $0.05^{\circ}$  of  $78.4^{\circ}$ . The acetone was purified by converting it into the sodium iodide compound, collecting, and distilling the double compound. The product was then carefully dried and fractionated twice, as in the case of the other compounds. The purity of the solvents used can be gauged from the fact that the acetone obtained had  $D_{4}^{20}$  0.7808, as low a figure as any published. These solvents were carefully preserved in a dark cupboard.

Except when otherwise specified, percentages can be taken to mean percentage by volume. Tubes are also often specified by their diameters. Thus a tube 5 cm. in diameter would be referred to as a 5 cm. tube.

### SECTION I.

#### *The Ignition-temperatures of Ether-Alcohol-Air and Acetone-Air Mixtures.*

With the exception of two figures for ether in air,  $1033^{\circ}$ , given by McDavid (T., 1917, **111**, 1003) and  $190^{\circ}$  by Alilaire (*Compt. rend.*, 1919, **168**, 729), the ignition-temperatures found in the literature for the solvents in question are spontaneous ignition-temperatures, which can be taken to be the temperatures at which the substances dealt with (surrounded by oxygen or air at the same temperature) will burst into flame without the application of any spark or other local high temperature. Two sets of these figures, which are intended for engine work, are given. Thus, Holm

(*Zeitsch. angew. Chem.*, 1913, 26, i, 273) gives the spontaneous ignition-temperature of alcohol in air as  $510^{\circ}$ , of acetone as  $570^{\circ}$ , and of ether as  $400^{\circ}$ . Moore (*J. Soc. Chem. Ind.*, 1917, 36, 109) gives the spontaneous ignition-temperatures of ether and alcohol in air as  $347^{\circ}$  and  $518^{\circ}$ , and in oxygen as  $190^{\circ}$  and  $395^{\circ}$  respectively. It will be seen that only the figure given for the ignition-temperature of ether in air by Alilaire, which was published after the completion of our work, appears to be sufficiently low to make an ignition of the solvent-air mixture under present-day conditions of recovery seem feasible.

A paper by Perkin (T., 1882, 41, 363) on the luminous, incomplete combustion of ether is interesting in this connexion. According to him, this phenomenon was first discovered by Davy, who noticed a pale phosphorescent light round a hot platinum wire. Doebereiner noticed the same thing, and also remarked that when ether was dropped into a retort heated on the sand-bath to  $100^{\circ}$  and upwards, or into a platinum capsule exposed to the vapour of boiling water, the spheroidal state is produced, accompanied by a blue flame visible only in the dark, and not capable of setting fire to other substances, lachrymatory vapours of lampic acid being formed.

Boutigny and Miller also noted this flame and the products of the combustion, and proved that metal or porcelain dishes were equally effective in producing these phenomena. Boutigny gives the temperature at which ether begins to burn with this flame as a little below that of fusing lead, and so agrees with Perkin and others that the temperature necessary must be about  $260^{\circ}$ . As will be seen later, however, a temperature much below this is sufficient to produce this flame in ether-air mixtures. According to Perkin, this blue flame has a comparatively low temperature (it has since been designated a "cool" flame). The fingers may be placed in it with impunity. It will neither char paper nor ignite carbon disulphide, and a lucifer match may be held in it for some time before being ignited. He also states, however, that ether vapour burning with this blue flame, when in large quantities, or more especially in a confined space, rapidly increases in temperature and quickly enters into ordinary combustion.

Perkin also examined other substances for "the luminous appearance accompanying incomplete combustion." Only traces of blue flame were obtained with the alcohols up to amyl, methyl alcohol giving none.

The generally accepted definition of ignition-temperature is that temperature to which a gas-mixture must be heated, at least locally, for the speed of the reaction to be such as to become self-support-

ing. This temperature is not that at which a flame appears, but that at which self-heating becomes sufficient to cause ultimate inflammation.

That the determination of an ignition-temperature is a matter of great difficulty can at once be seen when it is considered that the temperature at which such a reaction would become self-supporting must depend on the rate of dissipation of heat in the system as well as on many other factors. For instance, if the time taken to bring the gas-mixture up to the ignition-temperature is appreciable, the composition of the gas-mixture alters, and if a solid is in contact with the heated gases, even below their ignition-temperature, as proved by Bone and Wheeler (*Phil. Trans.*, 1906, [A], 206, 1) and by Meyer and Freyer (*Ber.*, 1892, 25, 622), the most divergent results are obtained for the amount of combination that takes place. From their work, the German investigators concluded that it was impossible to determine an ignition-temperature.

We decided to try the soap-bubble method described by McDavid (*loc. cit.*), and if that proved unsatisfactory, as was anticipated from Meunier's work (*Compt. rend.*, 1907—1912), to attempt to make use of a method in which the amount of heated surface brought into contact with the gas would be known, thereby eliminating the most obvious defect in the soap-bubble method as published. To this end, it was decided to pass the various gas-mixtures of which the ignition-temperatures were required into certain uniformly heated vessels. In this way, the temperature at which ignition could be obtained in each vessel would be known. By taking vessels of the same material having different ratios of surface to volume and plotting the ignition-temperature against surface per unit volume, it was anticipated that by extrapolation it would be possible to eliminate to a great extent disturbing variations due to surface action. The most obvious vessels to use were tubes of various diameters, and a series of these was accordingly chosen. It was quite realised that the longer time taken to heat a large bulk of gas would affect the results to some extent, but direct experiment, in which some of the products of combustion were introduced into the gas-mixture to be used, soon proved this to be almost negligible in the case of ether-air mixtures of ordinary concentration. It is to be noticed, however, that in this method the temperature determined has been called the sub-ignition-temperature—the minimum temperature at which combination in a gas-mixture becomes self-supporting. This appears to be the practical temperature required, as the phenomenon obtained may or may not give rise to ordinary combustion, depending on circum-

stances. Its identity with the ignition-temperature of a mixture depends entirely on what is understood by "ignition," and a "flame" in those cases in which cool flames are possible phenomena.

Heating a gas-mixture quickly to its ignition-temperature is always assumed to cause ultimate inflammation. In many cases, an ordinary flame, causing more or less complete combustion, cannot be obtained by heating a gas to its sub-ignition-temperature, and in those cases in which such a flame appears it is only produced through the "cool" flame of incomplete combustion. For a fairly concentrated ether-air mixture, the cool flame obtained is very similar in appearance to an ordinary flame, but for very dilute mixtures it becomes practically a travelling phosphorescent flow.

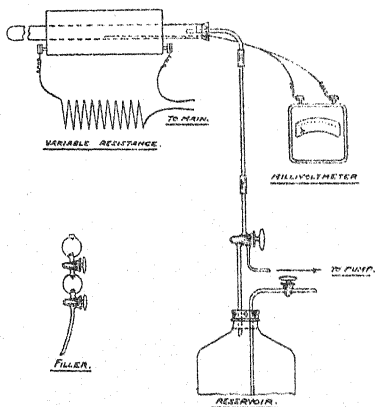
*The Soap-bubble Method.*—The results obtained during our investigation of the soap-bubble method of determining ignition-temperatures have already been published (this vol., p. 1248). By using different igniting surfaces, it was found that the ignition-temperature of a 5 per cent. ether-air mixture as determined by this method could vary from  $907^{\circ}$  to  $1064^{\circ}$ , whilst that of a 12 per cent. mixture could vary from  $870^{\circ}$  to  $1035^{\circ}$ . The results obtained seemed to be erroneous, and by using several gas-mixtures it was shown that the method could scarcely be trusted, even for comparative results.

*The Exhausted Tube Method.*—The apparatus used in this method is shown in Fig. 1. The heated vessel consisted of a long glass tube sealed at one end and closed at the other by means of a rubber stopper. The tube could be kept at any desired temperature by means of an electric furnace, the exact temperature inside the tube being registered by means of a copper-constantan couple except when that temperature was more than  $500^{\circ}$ , when a nitrogen-filled mercury thermometer was used. The ignition tube was connected to the glass reservoir containing the mixture under examination by means of a glass lead passing through the rubber stopper. A three-way tap was inserted between the tube and reservoir in such a manner that the tube and lead could be connected at will to the reservoir or to a Gaede box pump. The reservoirs were of 15 to 17 litres capacity, and the tubes used at first were a few cm. longer than the furnace, which was 50 cm. long. The reservoir was filled with any required mixture by exhausting it and allowing air to sweep a known weight of the solvent from the filler, shown in the figure. The filler was connected to the three-way cock by means of rubber tubing, but the end of the filler always projected into the tap tube. In this way, none of the solvent escaped introduction into the reservoir, and a knowledge of the molecular weight of the solvent, together with



the temperature and pressure, gave, by means of a simple calculation, the percentage volume occupied by the solvent in the reservoir. A portion of the lead between the three-way tap and the furnace was connected to the remainder by means of rubber joints. These joints enabled tubes of various internal diameters to be introduced in order to vary the rate at which equalisation of pressure in the tube and reservoir took place. An experiment was conducted as follows. The tube was exhausted to a pressure below 2 cm., and connected to the reservoir by turning the three-way cock as rapidly as possible; an observer, looking through the

FIG. 1.



sealed end of the tube (shielded by a plate of glass), reported whether ignition had or had not taken place.

*Shock Ignition.*—Preliminary experiments, using 5 to 15 per cent. mixtures of ether in air and a tube 2 cm. in diameter, gave results varying with the diameter of lead used. It was also found that changing the length of the tube from 50 to 100 cm. affected the temperature at which ignition was obtained. These irregularities were presumably due to the differences in time taken to fill the tube with the gas-mixture. Accordingly, a tube 7.5 cm. in diameter was substituted for the one previously used, so that the effect of changing the diameter of the lead could be investigated more easily. With a lead of 1 mm. diameter, ignition took place

at temperatures near  $200^{\circ}$ , but, on using a lead of 5 mm. in diameter, it was found possible to obtain ignition at from  $50^{\circ}$  to  $60^{\circ}$ . These results were obviously too low, and observation showed that they were influenced by the position of the end of the tube relative to the furnace. Experiments were carried out to elucidate this phenomenon, and it was found possible to ignite ether-air mixtures at the ordinary temperature and to ignite other gaseous mixtures at temperatures well below those commonly considered as their ignition-temperatures. The apparatus used consisted of a glass tube 7.5 cm. in diameter, which was connected to a reservoir of 16 litres capacity by means of a glass lead 80 cm. long and of 1.9 cm. internal diameter. By using on the reservoir a cock of 1.5 cm. bore, it was possible to equalise the pressure in the two portions of the apparatus very suddenly. Under these conditions, it was found that when the tube and lead were exhausted and kept at the same temperature as the reservoir ( $16.5^{\circ}$ ), ether-air mixtures containing 5 to 15 per cent. of ether were ignited on opening the reservoir cock.

The ignition invariably took place within 15 cm. of that end of the tube remote from the reservoir. In most cases it resulted in a pale blue flame, which travelled quietly along the tube, but sometimes gave inflammation sufficiently violent to shatter the glass. When using 7.5 cm. tubing, ignition could be obtained easily with 60 and 90 cm. lengths, even when the pressure in the reservoir was less than half the atmospheric. Ignition occurred in a 150 cm. tube only when the pressure in the reservoir was greater than three-quarters of an atmosphere. When a 300 cm. tube was used, no ignition could be obtained at the ordinary temperature; a similar negative result was obtained with bottles 30 cm. long and 11.2 to 12.5 cm. in diameter, that is, of approximately the same capacity as the 90 cm. tube. A pad of soft leather in the closed end of a tube of optimum length seemed to prevent ignition at the ordinary temperature, and a plug of cotton wool prevented ignition in precisely the same way. Replacement of the 7.5 cm. tube by one 2 cm. in diameter brought about the same result. It appeared to be immaterial whether highly purified ether or the ordinary commercial variety was used for these experiments. Amongst the other gases tested were mixtures of hydrogen and the vapours of acetone and carbon disulphide with air. Dilute carbon disulphide-air mixtures ignited at the ordinary temperature, acetone-air mixtures below  $250^{\circ}$ , and hydrogen-air mixtures below  $450^{\circ}$ , but these experiments were not continued. The information at present available makes it appear highly probable that this ignition is due to the shock caused by the sudden

stoppage of the gas rushing into the exhausted tube. In this connexion, a statement made by Sir Charles Parsons in his inaugural address at the Bournemouth Meeting of the British Association (1919) is of interest. This was to the effect that during the work of a committee appointed by the Admiralty in 1916 to investigate the cause of abnormal propeller erosion, it was discovered that by allowing water to rush into an exhausted conical vessel, a pressure of more than 220 kilos. per sq. mm. was recorded at the apex of the cone. That ignition of a gas-mixture can be produced by a compression wave was demonstrated by Bradshaw (*Proc. Roy. Soc.*, 1907, [A], 79, 236) for mixtures of carbon disulphide in oxygen and for electrolytic gas.

Another factor, the actual rarefaction, must not be forgotten. Investigations by Mitscherlich (*Ber.*, 1893, 26, 399) on the temperature necessary to explode mixtures of hydrogen and oxygen seem to show that the explosion point is reduced very appreciably by lowering the pressure. Again, Labillardiere, Friedel and Ladenburg, Stock and Guttman, and others have shown that the temperature necessary for the ignition of mixtures of the hydrogen compounds of phosphorus, silicon, and antimony with oxygen is presumably lowered by reducing the pressure, and that explosion has been known to follow sudden rarefaction. In the course of the work described in this paper, the maximum reduction in sub-ignition-temperature of ether-air mixtures apparently obtained by reduction in pressure alone was only  $7^{\circ}$ , that is, from  $187^{\circ}$  to  $180^{\circ}$ , as shown in Fig. 4. This appears to leave a fair margin for other factors.

The importance of this "shock" ignition is obvious whether it be considered from the theoretical or practical point of view, and it may quite well account for hitherto obscure ignitions met with in the course of solvent-recovery and mine work. The phenomenon underlying shock-ignition must also invalidate a good deal of research work.

*Attempt to Eliminate Shock-ignition.*—One conceivable method of avoiding shock-ignition in the determination of sub-ignition-temperatures would appear to be that in which the gas is given no appreciable flow before being stopped. An attempt to realise these conditions was made by joining a small bulb on to a gas reservoir in such a way that the distance between the bulb and reservoir was as small as possible. A three-way tap was inserted between the reservoir and bulb to enable the bulb to be exhausted before an experiment. The bulb, which was made of glass, was kept at any desired temperature by being almost entirely immersed in a bath of mercury. When once a connexion had been made

between the bulb and gas reservoir, the tap was turned so as to close both bulb and reservoir. If ignition took place, a flash was easily observed where the bulb-stem emerged from the bath. The bore of the bulb-stem was varied in different determinations. The results obtained when using a 4.5 per cent. mixture of ether in air are given in table I. From them, it will be noticed that the effect of the size of lead is not completely eliminated by this method.

TABLE I.

*Showing the Sub-ignition-temperatures of a 4.5 per cent. Ether-Air Mixture obtained by the Bulb Method, using Various Leads.*

Diameter of bulb in cm.	Sub-ignition-temperature when lead was		
	Ordinary tube.	Capillary.	Fine capillary.
4.8	178.0°	181.0°	184.0°
4.1	179.0	184.0	185.0
3.5	180.5	185.5	188.0

An interesting point observed in these experiments was the fact that when using a 4.5 per cent. mixture near its apparent ignition-temperature, explosion invariably occurred. On the other hand, when using the bulbs specified above with an ordinary capillary lead and the same gas-mixture, on no occasion did an explosion take place when the temperature of the bath was greater than 197°. Above this temperature, a luminous flash was observed, and nothing more. A 6 per cent. mixture gave similar results, but a 10 per cent. mixture gave no explosion at any temperature tried. An 8 per cent. mixture behaved in precisely the same way as a 10 per cent. mixture, except that on one solitary occasion a violent explosion shattered the bulb. It is possible that a good approximation to the correct sub-ignition-temperature could be obtained by using a very fine capillary tube and a fairly large bulb, but the experiment would not be without danger.

*Final Apparatus.*—It was found that by making use of a fairly long tube and allowing the sealed end to project well out of the furnace, effects of shock-ignition were apparently eliminated. In this case, the point at which shock-ignition would have occurred in normal circumstances was well outside the heated zone, and on no one occasion was an ignition in the final apparatus observed to start outside the furnace. The lengths of tube used were as follows:

2 cm. tube.	100 cm.
4 cm. tube.	130 cm.
5.5 cm. tube.	130 cm.

The chief difficulty encountered was that of deciding when an ignition had occurred. This was generally easy in the case of

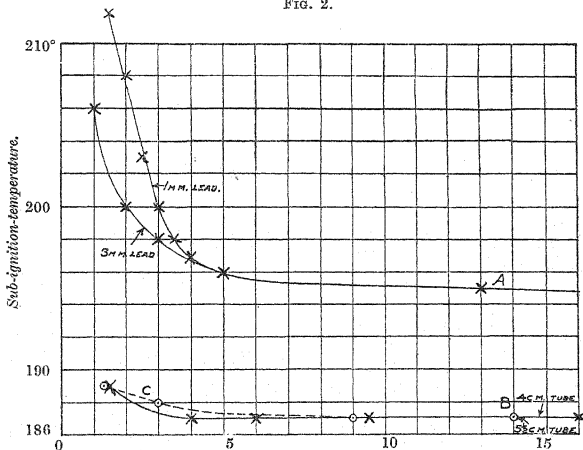
shock-ignition, as not only was the flame fairly easily seen, but the products of combustion had a characteristic and powerful odour. In the case of dilute mixtures of ether in air and ether-alcohol-air mixtures containing small quantities of ether, however, the matter was quite otherwise. It was found almost impossible to distinguish between an ignition and the glow given below the sub-ignition-temperature by combustion on the surface of the glass until travelling was taken as the criterion. This was, of course, due to the fact that the ignition at the lowest possible temperature of a mixture containing ether and air invariably commenced with what has been termed the cool flame. This flame often requires a completely darkened room in order to be visible, but whenever any appreciable quantity of combustible mixture is present, it is liable to develop more or less rapidly into ordinary combustion and, possibly, detonation. That the volume of mixture present is an important factor can be seen from the fact that on no occasion did ordinary combustion develop in the 2 cm. tube within  $150^{\circ}$  of the sub-ignition-temperature. On the other hand, when using mixtures containing from 5 to 10 per cent. of ether in either of the other tubes, ordinary combustion was liable to develop, and certainly did develop if the temperature was a few degrees above that necessary for inflammation. Test experiments carried out with and without the thermo-couple and thermometer in the tube showed that the presence of these instruments did not appear to affect the result obtained.

Fig. 2 gives the results obtained for the sub-ignition-temperatures of various ether-air mixtures. It will be noticed that in the case of the 2 cm. tube, the results for dilute mixtures differ slightly according to the lead used. This is presumably due to the fact that combustion takes place to a relatively greater extent in the case of the smaller lead, making it more difficult to see the flame at the same temperature. On the other hand, above a certain limit, the internal diameter of the lead does not appear to affect the results obtained with the other tubes. Surface action appears to be negligible in the case of ether-air mixtures of any appreciable concentration if the tube has a diameter of at least 4 cm. That the longer time taken to heat the larger bulk in a wide tube made little difference in the case of ether-air mixtures of concentration greater than about 4 per cent. was proved by adding 1.5 per cent. of the products of combustion of an ether-air mixture to a 5 per cent. mixture of ether in air. The sub-ignition-temperature was only raised  $2^{\circ}$ . It was found that no difference in sub-ignition-temperature could be detected when purified ether was replaced by the commercial article. It is interesting to note from the shape

of the curve in Fig. 2 that the ignition of ether-air mixtures by this method, depending as it does on the preliminary production of the cool flame, appears to be a molecular process requiring only a certain intensity of molecular movement for its production. The form of curve connecting minimum igniting current with composition of ether-air mixture appears to be quite different.

In Fig. 3 can be seen the sub-ignition-temperatures of certain ether-alcohol-air mixtures as determined in the 2 cm. and 4 cm.

FIG. 2.



Percentage of ether in mixture.

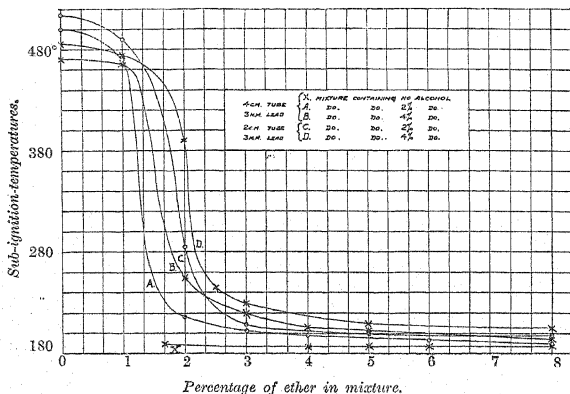
- A. 2 cm. tube, 1 and 3 mm. leads.
- B. 4 cm. tube, 3 mm. lead.
- C. 5 1/2 cm. tube, 3 mm. lead.

tubes. The number of points shown on each curve is not great, owing to the fact that the general form of the curves had been previously found when using smaller leads. Each point on the diagram is the mean of three determinations agreeing to within 2° in the case of temperatures below 220° and to within 5° in the case of temperatures above this point.

A consideration of the results given shows that the sub-ignition-temperature of an ether-alcohol-air mixture falls very rapidly when the amount of ether in the mixture is increased from 1 to 2

per cent. This drop is seen to take place with a smaller percentage of ether in the case of the 4 cm. tube, and in both tubes with a smaller percentage of ether in the case of the mixture containing the smaller amount of alcohol. The curves also indicate the manner in which the addition of alcohol to an ether-air mixture affects the sub-ignition-temperature. The elevation in sub-ignition-temperatures is roughly proportional to the amount of alcohol present provided the ether-content lies between 2 and 5 per

FIG. 3.



cent. For comparison, some results, obtained with 4 and 5.5 cm. tubes, are given in table II.

TABLE II.

*Showing the Sub-ignition-temperatures of Various Ether-Alcohol-Air Mixtures containing 2 per cent. of Alcohol, as determined in 4 and 5.5 cm. Tubes.*

Percentage of ether in mixture.	Sub-ignition-temperature for		
	5.5 cm. tube.		4 cm. tube. 3 mm. lead.
	5 mm. lead.	3 mm. lead.	
1	495°	500°	470°
2	220	222	217
3	207	210	203
5	201	205	197

The sub-ignition-temperature determined with the 5.5 cm. tube is seen to be higher in every case than that obtained with the 4 cm. tube. This is probably due to the fact that, owing to the larger diameter of this tube, the time of heating is necessarily longer, and hence slow combustion occurs more readily.

With this tube, too, a slight but perceptible difference in sub-ignition-temperature is obtained when using 3 mm. and 5 mm. leads, as shown in table II.

It was seen that in the case of dilute mixtures of ether in air the size of lead used, if small, affected the temperature obtained. This effect was exceedingly marked in the case of ether-alcohol-air mixtures containing little ether. With small leads, it was found impossible to obtain consistent results. For instance, for a mixture of 2 per cent. of alcohol and 1.25 per cent. of ether in air, when using a 1 mm. lead with the 4 cm. tube, a flash would occasionally be obtained below 300°, but one could only be certain of an ignition well above 400°. It was found, however, that if the cock connecting the tube and reservoir was turned on slowly, no ignition was ever obtained below 400°. These differences vanished when leads of 3 mm. or more were used.

The sub-ignition-temperatures of various alcohol-air mixtures are given in table III.

TABLE III.

*Showing the Sub-ignition-temperatures of Various Alcohol-Air Mixtures as determined in 2 cm., 4 cm., and 5.5 cm. Tubes.*

Percentage of alcohol in mixture.	Sub-ignition-temperature for		
	2 cm. tube (3 mm. lead).	4 cm. tube (3 mm. lead).	5½ cm. tube (5 mm. lead).
2	515°	500°	520°
3	505	490	505
4	485	470	500
5	480	465	495

In the 4 cm. tube an explosion was often obtained with 4 and 5 per cent. alcohol-air mixtures at 485°. The evidence as to the slower heating of the gaseous mixture in the largest tube is confirmed by the figures given here, as the temperatures found in the case of the largest tube are higher than those for the smallest. It thus appears from the above figures that the nearest possible approach to the correct sub-ignition-temperature of an ether-alcohol-air mixture is obtained by means of a 4 cm. tube. It was found that almost identical results were obtained in the 2 cm. and 4 cm. tubes, whether 2 or 3 mm. leads were used, and that it was not important whether a 3 or 5 mm. lead was used for the



5.5 cm. tube. The sub-ignition-temperatures considered most likely to be correct are summarised in table IV.

TABLE IV.

*Showing the Sub-ignition-temperatures of Various Ether-Alcohol-Air Mixtures.*

Percentage composition of mixture by volume.			Sub-ignition-temperatures.
Ether.	Alcohol.	Air.	
3—15	0	97—85	187°
8	2	90	189
4	2	94	198
3	2	95	203
2	2	96	217
1	2	97	470
8	4	88	194
4	4	92	206
3	4	93	220
2	4	94	255
1	4	95	465
0	2	98	500
0	3	97	490°
0	4	96	470
0	5	95	465

The sub-ignition-temperatures of some acetone-air mixtures as determined in tubes of various diameters were found to vary in a manner similar to those of alcohol-air mixtures. The results given below were obtained when using a tube 4 cm. in diameter with a 3 mm. lead.

TABLE V.

*Showing the Sub-ignition-Temperatures obtained for some Acetone-Air Mixtures.*

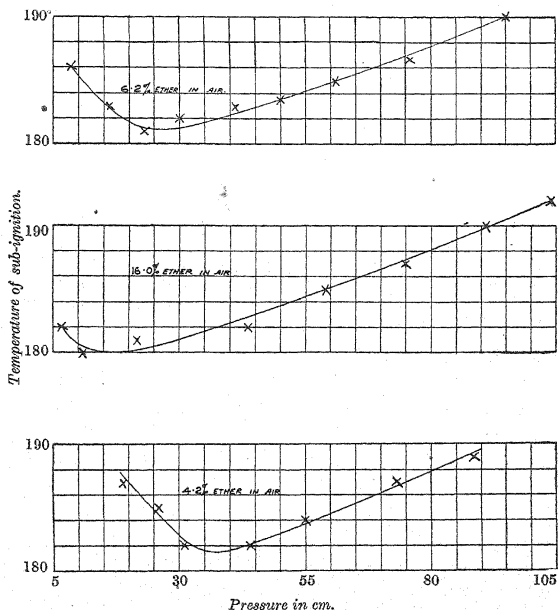
Percentage of acetone in acetone-air mixture.	Sub-ignition- temperature.
4	500°
8	500
Saturated at 15°	505

The ignition found for acetone was very faint at the sub-ignition-temperature, but grew in intensity very rapidly as the temperature of the tube increased.

*Influence of Pressure.*—During the course of preliminary work on the determination of sub-ignition-temperatures of ether-air mixtures, it was found that consistent results were not obtained for successive experiments when the mixture in the reservoir was not renewed after each determination. This was apparently due to change of pressure inside the reservoir. Several experiments

were therefore made in which the pressure in the reservoir was reduced by pumping out the gas-mixture before firing, and it was found that when the pressure in the reservoir after an experiment was plotted against the sub-ignition-temperature determined, the curves shown in Fig. 4 were obtained. Other mixtures tested in the same way gave precisely similar results, and it was finally found

FIG. 4.



that the easiest method of determining the accurate sub-ignition-temperature of any given mixture under 760 mm. pressure was by starting with a gas-mixture under about 900 mm. pressure and plotting a small portion of the pressure-sub-ignition-temperature curve. The results given in Fig. 2 were obtained in this way. It will be observed that the minimum sub-ignition-temperature

appears to be given at a lower pressure in the case of a mixture rich in ether than in the case of a dilute mixture. This is probably due to the fact that there is a minimum quantity of ether per unit volume necessary to give visible luminosity under any given conditions.

*Influence of the Material of the Tube.*—A consideration of the results obtained with various tubes shows that it was impossible to eliminate surface action entirely, probably owing to the fact that in the case of the larger tube the heating of a body of gas is necessarily slower. It thus became a matter of importance to discover whether the material of the tube had any influence on the result obtained. The simplest method of effecting this appeared to be by fitting a glass tube with a thin sleeve of the material under test. Accordingly, the 4 cm. tube was fitted with sleeves long enough to project beyond the furnace on either side, these sleeves being made of various metals that might conceivably be used in a manufacturing plant in the presence of gas-mixtures such as those considered. The results obtained are given in table VI.

TABLE VI.

*Showing the Results obtained for the Sub-ignition-temperature of Ether-Air and Alcohol-Air Mixtures in a 4 cm. Tube provided with an Internal Metallic Sleeve.*

Material of sleeve.	Sub-ignition-temperature.		
	4.3 per cent. of ether in air.	10.5 per cent. of ether in air.	5 per cent. of alcohol in air.
Glass .....	187°	187°	465°
Copper .....	175	175	420
Iron .....	178	178	400
Lead .....	180	180	—
Zinc .....	184	184	—
Galvanised iron .....	184	184	—

The figures given for copper and iron in the case of the alcohol-air mixture can only be regarded as rough approximations, owing to the rapidity with which these metals oxidised at the temperature necessary for ignition. When the metal was oxidised to any appreciable extent, different results were obtained. For instance, the sub-ignition-temperature in the case of a copper sleeve oxidised in the course of ten experiments was 470°. In the case of both ether-air and alcohol-air mixtures, the ignition commenced as a cool flame, but was invariably more violent in the presence of metals, more particularly copper and iron, than with glass.

*Influence of the Velocity of the Gas-mixture.*—As the gases dealt with in solvent-recovery are generally in motion, it was

decided to investigate to some slight extent the effect of the velocity factor on the sub-ignition-temperatures obtained. Arrangements were therefore made by which the gas-mixture in a reservoir could be displaced by means of water, and the gas from this reservoir made to displace the contents of a second reservoir. The gas-mixture from this second reservoir was passed into a 4 cm. tube 120 cm. long, which was kept at any desired temperature by means of an electric furnace. The far end was partly closed by means of a thick glass plate. It was found that once a steady state had been attained, the velocity of the gas in the tube could be measured sufficiently accurately by estimating the rate at which water was introduced into the first reservoir. An observer looking through the plate glass could easily see if ignition occurred. The sub-ignition-temperature for zero velocity was taken to be the lowest temperature at which ignition occurred after the gas supply had been cut off. The results obtained for two ether-air mixtures are given below in table VII.

TABLE VII.

*Showing the Effect of the Velocity of the Gas-mixture flowing through a 4 cm. Tube on the Sub-ignition-temperature observed.*

4.5 per cent. of ether in air.		14 per cent. of ether in air.	
Velocity in cm. per second.	Sub-ignition- temperature.	Velocity in cm. per second.	Sub-ignition- temperature.
0	187°	0	186°
6.0	195	1.0	189
12.5	202	5.5	195
—	—	8.0	197
—	—	13.0	202

The experiments carried out were sufficient to indicate that for very small velocities, increase of velocity causes an elevation of the sub-ignition-temperature observed. The velocities dealt with on the manufacturing scale are, however, of a totally different order, ranging from 100 to 400 cm. per second in various pipes.

*Influence of the Presence of Glyceryl Trinitrate, Ethyl Hydrogen Peroxide, and Diethyl Peroxide in the Ether Used.*—Several attempts were made to find if the presence of glyceryl trinitrate in an ether-air mixture affected the sub-ignition-temperature. In no case was any such effect discernible. In the experiments for which the results are given in table VIII, the glyceryl trinitrate was introduced into the reservoir by passing the air used for making up the mixture through a calcium chloride tube in which glyceryl trinitrate was spread over glass wool, the tube and contents being

kept at 40° to 45°. Results obtained in a 2 cm. tube were similar to those given below, which were determined by using a 4 cm. tube.

TABLE VIII.

*Showing the Effect of the Presence of Glyceryl Trinitrate, Ethyl Hydrogen Peroxide, and Diethyl Peroxide on the Sub-ignition-temperature of Ether-Air Mixtures.*

Composition of Mixture.	Sub-ignition-temperature.
5.3 per cent. of ether in air .....	187°
5.3 per cent. of ether and 1.5 per cent. of diethyl peroxide in air .....	189
3.7 per cent. of diethyl peroxide in air .....	189
4.7 per cent. of ether and 0.5 per cent. of ethyl hydrogen peroxide in air .....	182
5.3 per cent. of ether in air saturated with glyceryl trinitrate at 20° .....	187

The presence of glyceryl trinitrate did not appear to affect the flame given by the mixture, but the presence of the peroxides caused a very fierce flame and generally an explosion.

It was considered inadvisable to try to determine the sub-ignition-temperature of ethyl hydrogen peroxide in air. The peroxides were found to be exceedingly dangerous to handle; even diethyl peroxide exploded violently on one occasion during distillation.

## SECTION II.

*The Limits of Propagation of Flame in Ether-Alcohol-Air and Acetone-Air Mixtures.*

Many references are to be found in the literature to the limits of inflammability of mixtures of ether and alcohol with air, and some figures are also given for acetone-air mixtures. The limits determined by various workers are given below.

*Ether-Air Mixture.*—Limits of inflammability.

2.7 to 7.7 per cent. by volume (Brunswig, "Explosives," first edition, 1912, p. 73).

50 to 60 grams per cubic metre for lower limit (Marchis, *Met. and Chem. Eng.*, 1916, 14, 190).

2.9 to 7.5 per cent. by volume (Lewes, *J. Soc. Arts*, 1915, 761).

2.9 to 7.5 per cent. by volume (Schwartz, "Fire and Explosion Risks," first edition, p. 35).

0.058 to 0.195 gram per litre (Meunier, *Compt. rend.*, 1907, 144, 1107).

*Alcohol-Air Mixture.*—Limits of inflammability.

4.0 to 13.7 per cent. by volume (Brunswig, *loc. cit.*).

4.0 to 13.6 per cent. by volume (Lewes, *loc. cit.*).

3.95 to 13.65 per cent. by volume (Bunte and Eitner, *J. Gasbeleucht*, 1901, **44**, 835).

3 to 8.4 per cent. by volume (Thornton, *Proc. Roy. Soc.*, 1914, [A], **90**, 280).

*Acetone-Air Mixture.*—Limits of inflammability.

5 to 12 per cent. by volume (Brunswig, *loc. cit.*).

2.15 to 9.7 per cent. by volume (Wheeler and Whitaker, *T.*, 1917, **111**, 267).

It will be seen that the results obtained vary considerably, owing to the different conditions under which the experiments were carried out and the various igniting sources used. This is to be expected, as the conditions governing the propagation of flame were not properly appreciated until recent years. The definition now adopted is that suggested by Coward and Brinsley (T., 1914, **105**, 1859), in which inflammability is regarded as a specific property of a mixture, independent of the size and shape of the vessel in which it may happen to be contained, and also of any particular type of igniting arrangement. They propose to define a gaseous mixture as inflammable *per se* at a stated temperature and pressure if, and only if, it will propagate flame indefinitely, the unburnt portion of the mixture being maintained at the original temperature and pressure. On this definition, inflammability is a property of the mixture itself, although a function of the temperature and pressure. Dilution-limits, however, rarely vary much throughout the usual range of variation of laboratory temperature and pressure. It will thus be seen that, in order to obtain satisfactory results in the estimation of dilution-limits, it is necessary to use a vessel (1) of such size that any cooling of the gas-flame by the walls can be neglected, and (2) of sufficient length to enable a sound judgment to be made as to whether a flame would propagate indefinitely or no.

For every gas-mixture examined, propagation-limits were determined for three directions—upward, horizontal, and downward.

Preliminary work seemed to indicate that in a glass tube 5 cm. in diameter, by using a sufficiently powerful initiator, it was possible to force a flame through a mixture below the limit of propagation to the end of the tube, unless it was at least 120 cm. long. All the tubes for limit work were therefore made at least 150 cm. in length.

The tubes consisted of:

(1) Glass tubes 2.5 cm. in diameter.

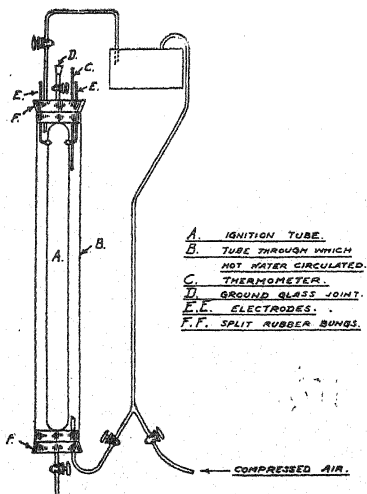
- (2) Glass tubes 5 cm. in diameter.\*
- (3) An iron \* tube 5 cm. in diameter.
- (4) An iron tube 15 cm. in diameter and 300 cm. long.

The glass tubes and the 5 cm. iron tube were 150 cm. long. The glass tubes were closed at both ends by gas-tight stopcocks of 4 mm. bore, and a similar cock was fitted to one end of the iron tube, where a 5 cm. glass observation piece was cemented for observation purposes. The cocks, in the case of the 15 cm. iron tube, were of brass and of 6 mm. bore. In this tube, inflammation was observed through three equidistant windows of thick plate glass, which were cemented into holders on the tube. These windows gave much trouble, and it was found impossible to render them gas-tight by using cement alone. Accordingly, caps were soldered over each window in such a way that, by inserting a 3.7 cm. rubber stopper into the observation hole left in the cap, the whole apparatus could be made gas-tight. The stoppers were removed immediately before firing. This tube was filled by means of a filler similar to that shown in Fig. 1, the end of the filler being made to project well through a tightly fitting piece of rubber tubing drawn over one of the cocks. The filling was carried out precisely as described previously, a correction being always applied for the vapour of the solvent present in the air above the liquid in the filler. In the case of all the smaller tubes, the fillers were provided with ground-glass joints fitting pieces sealed on to the tubes concerned. All the air passed in to make up any mixture containing alcohol or acetone was carefully dried by passage through a calcium chloride tube. The calibration of the tubes was carried out by weighing the quantity of water necessary to fill them. Ignition was effected by passing a spark from an induction coil between two electrodes of stout platinum wire separated by an air gap of 1 cm., the current being obtained from six 2-volt accumulators. In the glass tubes originally used, the platinum was sealed through the glass, but as good sealing glass became scarce, this was found to be impracticable, and the electrodes used for all the tubes consisted of platinum in glass mounted in rubber stoppers. The original method of mixing the gases was by allowing the tube to remain for several hours, but this became inadvisable when rubber was brought into contact with the solvent-laden air. A little mercury enabled efficient mixing to be carried out by shaking the tube, but it was found that this affected the results obtained, and, finally, small glass beads were used. Com-

\* This, and the other iron tubes used in the investigation, consisted of terne-plate, that is, sheet-iron coated with an alloy of lead and tin.

parative tests showed that, when using an adequate number of beads, shaking a 5 cm. tube for twenty minutes gave satisfactory mixing. It was also shown that, under these conditions, the same results were obtained whether the electrodes were held by small rubber stoppers or were sealed through the glass. Throughout the course of the work, the only tube that caused trouble was the 5 cm. iron tube. The various cements used for fastening the glass observation cap to the main body of the tube seemed to hold solvent, and the results obtained for this tube cannot be considered

FIG. 5.



as trustworthy as those obtained with the others. The mixing of the contents of the 15 cm. iron tube was done very efficiently by rolling a 12.5 cm. perforated hollow copper ball from end to end.

The apparatus used for determining the upper limit of propagation for alcohol-air and certain ether-alcohol-air mixtures consisted of a 5 cm. glass tube jacketed by enclosure in a wider glass tube, so that hot water could be continuously circulated round it. The arrangement used is shown in Fig. 5.

Two sets of this apparatus were fitted up, one as shown in the



sketch, arranged for experiments on downward propagation, with the electrodes at the same end of the tube as the ground-glass joint for filling the tube, and the other arranged for upward propagation, in which the electrodes were at the end away from the ground-glass joint. For horizontal propagation, either of the above tubes was used and placed horizontally before firing. Some difficulty was encountered in sparking the mixtures contained in this apparatus, but by enclosing the leads in glass tubes, this was finally overcome. Naturally, mixing in these tubes could only be accomplished by allowing the tube to remain for some time.

The procedure in the case of any mixture can be seen by a consideration of the results given below.

*Experiment 21.*—Glass tube, 5 cm. in diameter.

Solvent mixture used, 75 per cent. of ether and 25 per cent. of alcohol (by weight).

Lower limit, downward propagation. Temperature, 19°.

Percentage of solvent-vapour in gas-air mixture (by volume).

2.70	.....	Complete ignition.
2.40	.....	Flame just started.
2.60	.....	Complete ignition.
2.50	.....	Partial ignition.
2.55	.....	Flame went nearly to the end.
2.57	.....	Flame went very slowly to the end.

Limit—2.57 per cent.

In the case of a lower limit, an accuracy of 0.02 per cent. was aimed at; in the case of an upper limit, 0.05 per cent. was taken. In every instance, just before firing, the cock furthest removed from the electrodes was opened to allow a free passage for the gases. When the limit of propagation was being determined for a mixture of ether and alcohol, a liquid containing the requisite proportions of these two solvents was made up and used. A test experiment showed that this gave the same result as was obtained when the two solvents were weighed into the tube separately.

*Ether-Alcohol-Air Mixtures.*—The results obtained for ether-alcohol-air mixtures in glass tubes are shown in table IX.

The experimental results obtained with the 2.5 cm. tubes are not so trustworthy as those determined in larger tubes, as can be seen from the results themselves. For example, the result obtained for the lower limit of an ether-air mixture is least for downward propagation, and other anomalies could be pointed out in the same way. These irregular results were probably due to the fact that it was only for downward propagation that the flame travelled more or less steadily. For upward propagation, it was sometimes

TABLE IX.

*Showing the Limits obtained for the Propagation of Flame in Ether-Alcohol-Air Mixtures as determined in Glass Tubes.*

The limit figures given show the percentage volume occupied by the total ether-alcohol vapour.

Percentage composition of mixture (by weights).		Diameter of tube in cm.	Upwards.			Horizontally.			Downwards.	
			Upper limit. Per cent.	Lower limit. Per cent.		Upper limit. Per cent.	Lower limit. Per cent.		Upper limit. Per cent.	Lower limit. Per cent.
Ether.	Alcohol.									
100	0	2.5	18.50	2.35		6.15	2.38		6.30	2.34
75	25	"	6.95	3.15		7.35	3.36		7.35	2.99
50	50	"	—	3.52		—	3.39		—	3.58
25	75	"	—	4.35		—	4.45		—	4.40
0	100	"	—	5.02		—	5.18		—	5.21
100	0	5	15.75	1.93		8.00	2.05		6.15	2.15
75	25	"	11.70*	2.40		10.95*	2.49		8.35*	2.57
50	50	"	10.70*	2.89		10.35*	2.99		9.25*	3.05
25	75	"	12.00*	3.53		11.50*	3.61		10.35*	3.71
0	100	"	18.95*	4.24		13.80*	4.32		11.50*	4.44

\* The figures marked thus were determined in the jacketed tube at 60°, and are, for this reason, not strictly comparable with the others, which were determined at air-temperature (20° ± 2°).

obviously jerked out. Wheeler's work has shown that only a very slight change in the limits takes place when the diameter of the glass tube is increased beyond 5 cm., so that this was the largest size of glass tube used. His work, however, was chiefly carried out with permanent gases.

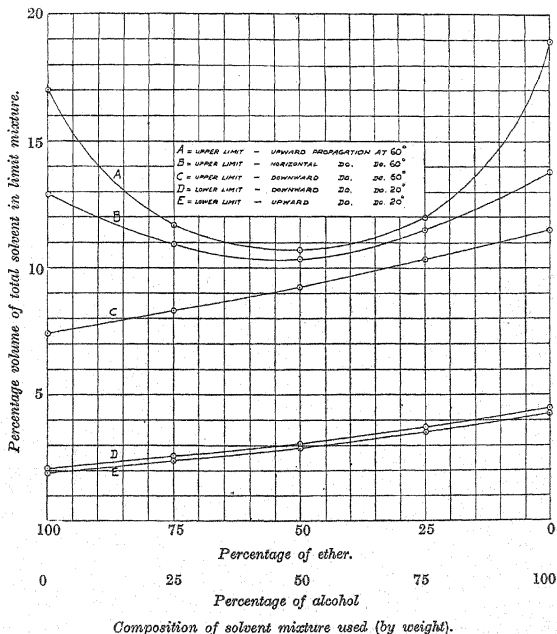
The most noticeable fact brought out in table IX appears to be the great difference between the results obtained for the upper limit for upward propagation and those obtained for propagation in other directions. These differences, which are normally due to convection currents set up by the flame, are not so great for permanent gases. The difference between the upper limits for horizontal and for upward propagation is most marked, and it almost appears as if a different type of propagation were brought into being. It is quite conceivable that the heated gases, rising in the tube, are responsible for the initiation of a cool flame. The difference is not so great in the case of alcohol as it is for ether.

The results for ether-alcohol-air mixtures in a 5 cm. glass tube are shown in Fig. 6. The results given for the upper limits were all determined at 60°. The graphed results for the lower limits and the upper limit for downward propagation form good approximations to straight lines, but this is not the case for the other two curves. At first sight, it seems very strange that, for the upper limit for upward propagation, the results for a mixture containing equal weights of ether and alcohol should be more than 6 per cent. less than the corresponding figure for either ether or alcohol. A possible explanation appears to be afforded by an examination of the sub-ignition-temperature curves given in Fig. 3. From these, it will be seen that the addition of alcohol to an ether mixture raises the sub-ignition-temperature so that the slope of the two upper curves near the 100 per cent. ether point is in the direction to be expected. Similarly, the slope near the 100 per cent. alcohol point can be explained when it is remembered that it takes an appreciable quantity of ether to cause any decided lowering of the sub-ignition-temperature of an ether-alcohol-air mixture. That there is no apparent irregularity corresponding with that seen when the percentage of ether is between 1 and 2 per cent. on the sub-ignition-temperature curves may be due to the fact that so few points have been determined on the limit curve; but it is far more likely to be due to the fact that the sub-ignition-temperature obtained for an ether-alcohol-air mixture containing, say, 2 to 2.5 per cent. of ether, is due solely to the ignition of the ether present, and that the alcohol takes little part in the reaction. These remarks do not apply to curve *C*, Fig. 6,

as in that case the flame obtained is undoubtedly that of ordinary combustion.

The limits of inflammability of a mixture of two or more gases with air are connected with the limits of the components of the mixture by Le Chatelier's rule, which states that if  $n, n', n'' \dots$

FIG. 6.



are the percentages of various combustible gases in a limit mixture which will just propagate flame, and  $N, N', N'' \dots$  the limiting percentages of the separate gases that can propagate flame, then

$$\frac{n}{N} + \frac{n'}{N'} + \frac{n''}{N''} + \dots = 1.$$

In table X are given the values for Le Chatelier's constant,

calculated from the results found for various ether-alcohol-air mixtures in 5 cm. glass tubes.

TABLE X.

*Showing the Value obtained for Le Chatelier's Constant for Various Ether-Alcohol-Air Mixtures in 5 cm. Glass Tubes at  $20 \pm 2^\circ$ .*

Limit.	Direction of propagation.	Value of constant in mixture of following percentage composition by weight.			Maximum percentage variation from unity.
		25 ether. 75 alcohol.	50 ether. 50 alcohol.	75 ether. 25 alcohol.	
Upper	Downwards	0.984	0.971	0.983	3
	Horizontal ...	0.833	0.774	0.830	33
	Upwards ...	0.646	0.589	0.663	41
Lower	Downwards	0.989	0.967	0.980	3
	Horizontal ...	0.995	0.985	0.992	1
	Upwards ...	1.004	0.993	1.007	1

The figures used for the upper limits in this table were all found at  $60^\circ$ , those for the lower being determined, as usual, within  $2^\circ$  of  $20^\circ$ . It will be seen that in all cases for the lower limit and for downward propagation in the case of the upper limit, Le Chatelier's rule holds for mixtures of ether and alcohol with air, and consequently the limits for a mixture containing any proportion of ether and alcohol can be calculated with an error of not more than 3 per cent. For horizontal and upward propagation, however, the rule breaks down entirely. As would be expected, the greatest deviation from the rule always occurs for a 50 per cent. mixture.

In table XI are given the results obtained when the same mixtures were ignited in 5 cm. and 15 cm. iron tubes. The upper limits for ether-air mixtures are given in table XII.

TABLE XI.

*Showing the Results obtained in Iron Tubes of 5 and 15 cm. Diameter for the Lower Limits for the Propagation of Flame in Certain Ether-Alcohol-Air Mixtures at  $20 \pm 3^\circ$ .*

Percentage composition of solvent mixture by weight.		Diameter of tube in cm.	Lower limits for propagation of flame.		
Ether.	Alcohol.		Upwards.	Horizontal.	Downwards.
100	0	5	2.24	2.29	2.34
100	0	15	1.73	1.80	1.93
75	25	15	2.24	2.30	2.46
50	50	15	2.81	2.89	3.02
25	75	15	3.48	3.53	3.69
0	100	15	4.16	4.23	4.37

TABLE XII.

*Showing the Upper Limits for Propagation obtained for Ether-Air Mixtures in 5 and 15 cm. Iron Tubes.*

Diameter of tube.	Value of limit and direction of propagation.		
	Upwards.	Horizontal.	Downwards.
5	15.45	7.95	6.70
15	23.30	22.30	6.50

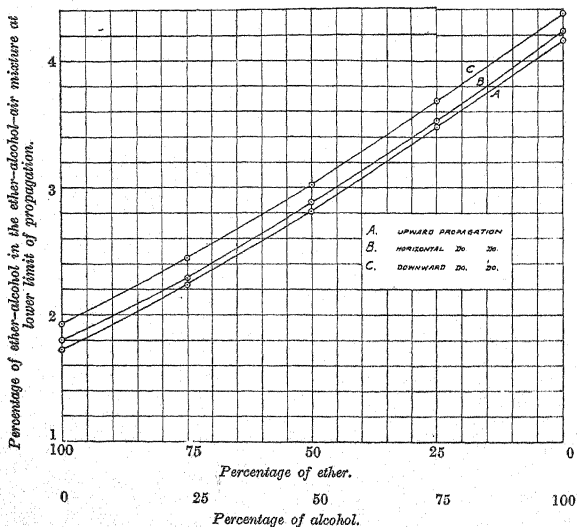
A comparison of these results with those given in table IX shows that for all three directions of propagation, the lower limit, as found for 5 cm. tubes, is greater when the tube is made of iron, as would be expected from the greater conductivity of this material. The reverse relation holds in the case of the upper limit obtained for ether-air for upward and horizontal propagation, but in the case of the downward propagation, the figure obtained for the iron is greater than that obtained for a glass tube of a similar size, or even for the 15 cm. iron tube. As this result appeared peculiar, a fresh determination of this limit was made, but the composition of the limiting mixture was found to be the same as that found in the first experiment. A comparison of the limits obtained in the 15 cm. iron tube with those previously determined (see tables IX, XI, and XII) is instructive. It will be seen that, in every case, the lower limit of a mixture is least in the case of the 15 cm. tube. The difference is very appreciable where a mixture contains a fair amount of ether, but is not so great where alcohol is present in excess. The upper limit, again, is always found to be greatest in the case of the 15 cm. tube, if we except the anomalous result obtained for downward propagation determined in the 5 cm. iron tube. These results may be due to a decrease in the cooling effect of the walls, or may possibly be due to turbulent motion in the gas caused by convection currents, as found by Wheeler and Mason (T., 1917, 111, 1044) in the case of velocity of flame. An item in favour of the latter supposition is provided by the exceedingly high figure obtained for the upper limit for horizontal propagation in the 15 cm. tube. On the other hand, the flame observed in the case of upward and horizontal propagation in the 15 cm. tube resembled very closely the cool flame of ether, and the characteristic odour following such a flame was observed. The lower-limit results for iron tubes are shown graphically in Fig. 7. The figures in table XIII show that Le Chatelier's rule holds moderately well for the lower-limit results obtained in the 15 cm. iron tube.

TABLE XIII.

Showing the Value Found for Le Chatelier's Constant from the Figures obtained for the Lower Limit for Propagation, using Ether-Alcohol-Air Mixtures in the 15 cm. Iron Tube.

Direction of propagation.	Values of constant given by mixture of percentage composition by weight shown.			Percentage maximum variation from unity.
	25 ether. 75 alcohol.	50 ether. 50 alcohol.	75 ether. 25 alcohol.	
Downwards .....	1.028	1.025	1.026	3
Horizontal .....	1.028	1.036	1.022	4
Upwards .....	1.039	1.038	1.031	4

FIG. 7.



Composition of the ether-alcohol mixture used (by weight).

*Acetone-Ether-Air Mixtures.*—Owing to the differences in results obtained for 5 cm. glass and 15 cm. iron tubes, particularly for ether-air mixtures, it was decided to determine the propaga-

tion of flame limits of certain ether-acetone-air mixtures in glass and iron tubes, as it was considered likely that results differing from those published by Wheeler and Whitaker (*loc. cit.*) for acetone-air mixtures would be obtained. The results of our experiments are shown in table XIV, those of Wheeler and Whitaker being given in table XV.

TABLE XIV.

*Showing the Propagation of Flame Limits obtained for Acetone-Ether-Air Mixtures, using Various Iron and Glass Tubes at  $20 \pm 2^\circ$ .*

Percentage composition of mixture by weight.		Material and diameter of tube.	Percentage of solvent in limit mixture and direction of propagation.					
			Upwards.		Horizontal.		Downwards.	
			Upper limit.	Lower limit.	Upper limit.	Lower limit.	Upper limit.	Lower limit.
0	100	Iron 5 cm.	—	3.80	—	3.90	—	4.00
0	100	Iron 15 cm.	12.40	2.88	12.40	2.89	10.90	3.11
0	100	Glass 5 cm.	12.20	2.89	9.15	3.04	8.35	3.15
25	75	„	11.20	—	8.55	—	7.75	—
50	50	„	11.70	2.34	8.25	2.39	7.25	2.49
75	25	„	13.20	—	8.15	—	6.65	—
100	0	„	15.75	1.93	8.00	2.05	6.15	2.15

TABLE XV.

*Showing the Propagation of Flame Limits as determined by Wheeler and Whitaker for Acetone-Air Mixtures in Glass Tubes of Various Diameters.*

Diameter of tube in cm.	Percentage of acetone in limit mixture and direction of propagation.					
	Upwards.		Horizontal.		Downwards.	
	Upper limit.	Lower limit.	Upper limit.	Lower limit.	Upper limit.	Lower limit.
2.5	7.5	2.30	6.7	2.40	6.5	2.75
5.0	9.5	2.20	9.3	2.25	8.3	2.40
10.0	9.7	2.15	9.5	2.20	8.5	2.35

It will be seen that our results differ considerably from those previously published. In most cases, they are considerably higher.



The explanation is almost certainly to be found in the fact that in our method the solvent was weighed directly into the tube, whilst in the other the acetone present in any mixture was estimated by analysis. That our method is the more accurate, as well as the easier, is obvious, but such a large discrepancy can only be explained by some abnormality in the behaviour of acetone during storage if the methods of analysis employed were not faulty. That such abnormal behaviour does take place when acetone vapour is stored over mercury is rendered extremely probable when the facts underlying the molecular association of acetone suggested in the paper by Wheeler and Whitaker are considered.

In this connexion, too, a quotation from the above paper might prove instructive. When discussing the analysis of the mixtures used, the following statement is made: "A supply of air was saturated with acetone vapour at 15° and 760 mm., when it contained 13·5 per cent. (by volume) of acetone, and used as a stock mixture from which the experimental mixtures could be prepared by the addition of air. . . . Consistent results were obtained by either of the absorption methods of analysis. Thus, a mixture, *known to contain about 6·5 per cent. of acetone*, gave on analysis:

"(1) Sodium hydrogen sulphite method . . . 6·50, 6·45, 6·54, 6·55.

"(2) Distilled water . . . 6·40, 6·56, 6·54, 6·50, 6·51, 6·51.

"Absorption by distilled water seemed, therefore, to afford a sufficiently accurate method of analysis."

The mixture "known to contain about 6·5 per cent. of acetone" was apparently made up by diluting the requisite quantity of the stock solution with a calculated volume of air. The accuracy of the method of analysis appears to be assumed from the fact that results approximating closely to the calculated figure were obtained. An examination of published figures for the vapour pressure of acetone at 15°, however, shows that a stock solution of air saturated with acetone vapour at this temperature at 760 mm. pressure would contain more than 19 per cent. of acetone (by volume), the vapour pressure of acetone at 15° being given by Sameshima (*J. Amer. Chem. Soc.*, 1918, **40**, 1482) as 147 mm. Extrapolation from Regnault's results gives a very similar figure—about 150 mm. Raising Wheeler and Whitaker's results in the ratio of 19:13·5 would often bring them much nearer to those obtained by us.

The results obtained for lower limits in the 15 cm. iron tube are strikingly similar to those obtained in a 5 cm. glass tube (see table XIV), and for upward propagation the upper limits are also very near. There are, however, very marked differences in the other figures given for the upper limits. It is worthy of note that

the upper limits for upward and horizontal propagation are here identical in the case of the 15 cm. tube. The results obtained when using the 5 cm. iron tube show clearly what a large effect the conductivity of the material of the tube has in this case. The results obtained in 5 cm. glass tubes for the propagation of flame limits of ether-acetone-air mixtures are shown graphically in

FIG. 8.

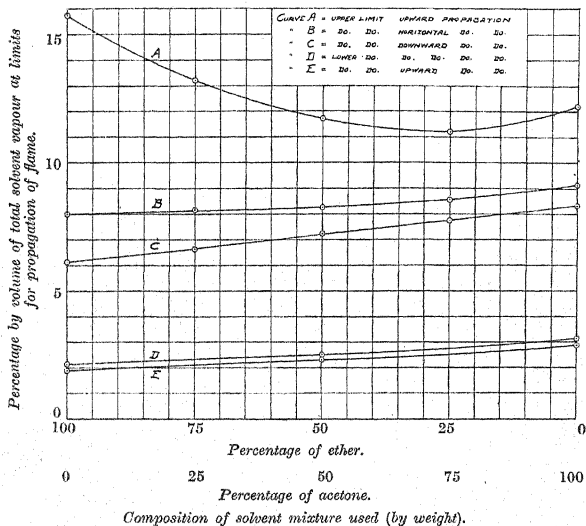


Fig. 8. It will be noticed that the upper-limit curves present the peculiarities commented on in the case of ether-alcohol-air mixtures, although to a less extent.

The figures given in table XVI show that Le Chatelier's rule holds moderately well for ether-acetone-air mixtures, except in the case of the upper limit for upward propagation.

TABLE XVI.

*Showing Values obtained for Le Chatelier's Constant for the Limits for Propagation, using Ether-Acetone-Air Mixtures in the 5 cm. Glass Tube at  $20 \pm 2^\circ$ .*

Limit.	Direction of propagation.	Value of constant given by mixture of percentage composition by weight shown.			Percentage [maximum variation from unity.
		25 ether. 75 acetone.	50 ether. 50 acetone.	75 ether. 25 acetone.	
Upper	Downwards	0.997	1.005	0.997	1
Upper	Horizontal	0.962	0.959	0.981	4
Upper	Upwards	0.875	0.866	0.910	13
Lower	Downwards	—	0.952	—	5
Lower	Horizontal	—	0.953	—	5
Lower	Upwards	—	0.987	—	1

*Influence of Temperature.*—The influence of temperature on the limits of inflammability of gaseous mixtures has been studied by Bunte and Roszkoski (*J. Gasbeleucht.*, 1890, **33**, 491, 524, 535, 553), Taffanel (*Compt. rend.*, 1913, **157**, 595), Burrell and Robertson (*United States Bureau of Mines, Technical Paper No. 121*, 1916), and Mason and Wheeler (*T.*, 1918, **113**, 45). The experimental work of Bunte and Roszkoski appears to have been defective, but the other workers found that the inferior limit of inflammability of methane-air mixtures was lowered by increasing the temperature of the gas-mixture before ignition. Mason and Wheeler also showed that the upper limit of inflammability of methane-air mixtures became much greater under these conditions, so that increasing the original temperature of the gas widens the limits of inflammability of methane-air mixtures. This would be expected from the fact that the self-propagation of a flame through a combustible mixture is only possible when the heat due to the reaction between the combining gases is sufficient to make up for losses due to radiation, conduction, and convection, whether the heat lost is dissipated or utilised in raising adjacent layers of the gas to the inflammation temperature. The heat of reaction necessary and the heat dissipated must obviously be less in the case where the original temperature of the gaseous mixture is higher. A few figures are given below to show to what extent the limits of inflammability are affected by temperature.

TABLE XVII.

*Showing some Results obtained by Mason and Wheeler for the Downward Propagation of Flame in Mixtures of Methane and Air.*

Initial temperature.	Lower limit.	Upper limit.
20°	6.00	13.40
100	5.45	13.50
200	5.05	13.85
300	4.40	14.25
500	3.65	15.35
700	3.25	18.75

In the circumstances, it was decided that it would be unnecessary to do more than find the change in the upper limit of ether-air mixtures with temperature. These experiments were carried out in the jacketed tube utilised for the upper limits of alcohol and ether-alcohol-air mixtures. The results obtained are shown in table XVIII. It will be seen that a decided rise in the upper limit for propagation takes place when the initial temperature of the mixture is raised through 40°.

TABLE XVIII.

*Showing how the Upper Limit for the Propagation of Flame Varies with the Initial Temperature of the Ether-Air Mixture Used.*

Direction of propagation.	Limit at 20°.	Limit at 60°.
Upwards .....	15.75	17.05
Horizontal ...	8.00	13.00
Downwards ...	6.15	7.45

*Influence of Pressure.*—The influence of pressure on the limits of inflammability of gases over any large range is by no means easy to predict, although it is well known that the lower limit of inflammability of many gas-air mixtures increases at diminished pressures. Terres and Plentz (*J. Gasbeleucht.*, 1914, 57, 990, 1001, 1016, 1025), Burrell and Robertson (*loc. cit.*), and Mason and Wheeler (*loc. cit.*) have investigated the effect of pressure on the limits of inflammability of mixtures of methane with air. The general conclusions to be drawn from their work appear to be that, below atmospheric pressures, decreasing the pressure narrows the limits of inflammability, but that above atmospheric pressure, increasing the pressure raises both the limits of inflammability.

The work done by us was confined to pressures at or below atmospheric pressure, and the results are shown in table XIX and XX.

TABLE XIX.

*Showing the Influence of Pressure on the Limits for Horizontal Propagation of Flame in Ether-Air Mixtures.*

Pressure in mm.	Percentage of ether in mixture.	
	At lower limit.	At upper limit.
770	1.87	—
751	—	12.90
600	—	10.50
520	—	9.20
460	1.88	—
450	—	8.20
420	—	7.90
400	—	7.80
300	1.92	7.30
200	2.08	6.80
100	2.33	6.10
50	2.99	5.00

TABLE XX.

*Showing the Influence of Pressure on the Limits for Downward Propagation of Flame in Ether-Air Mixtures.*

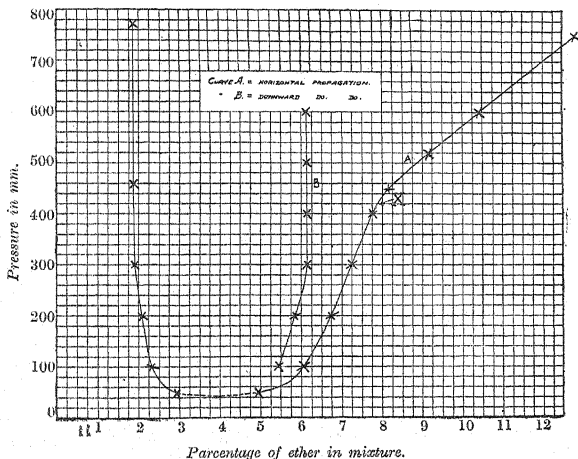
Pressure in mm.	Percentage of ether in mixture at lower limit.
600	6.20
500	6.20
400	6.20
300	6.20
200	5.90
100	5.50
50	No ignition.

It will be noticed that the results obtained near atmospheric pressure in the case of these experiments differ appreciably from those found by the ordinary method as given in table IX. This is due to the fact that all the experiments given in tables XIX and XX were carried out with both cocks closed. The type of ignition obtained was also very different; for instance, the ignitions obtained when determining the upper limit for horizontal propagation under 600 and 751 mm. pressure were characteristic, slow, cool flames which could not be seen except in a totally darkened room. It was found that any attempt to determine the limits for propagation of ether-air mixtures for pressures greater than atmospheric in the glass tubes available merely shattered the tube. The curves given by plotting pressure against the percentage of ether in the limiting mixture are given in Fig. 9. That for horizontal propagation is interesting. It was at pressures above that at the peculiar bend marked  $\times$  that the cool flame became notice-

able. Below this pressure the flame was of a green colour and traversed the tube very rapidly in a manner similar to that noticed for the lower limit at corresponding pressures.

*Influence of Velocity.*—Under present-day conditions of solvent-recovery, a good portion of the solvent-air mixture is often in rapid motion. It therefore became a question of determining, so far as was possible in the laboratory, the effect of velocity on the limits of propagation of solvent-air mixtures. Owing to the fact that no

FIG. 9.



real approximation to manufacturing conditions could be attained, the work done was confined to ether-air mixtures.

It has long been known that a moving mixture of combustible gas and air, too weak to propagate flame, can carry a cap of flame to a great distance from an igniting source. Wheeler has also proved that a mixture below the lower limit of propagation, when in a quiescent state, can often inflame when agitated. The speed of propagation of flame is also notably dependent on the degree of mechanical agitation of a mixture, and various experiments on the effect of agitation on gas-mixtures and on the rate of development of pressure when gas-mixtures are ignited are given by Clerk and

Hopkinson (*Rep. Brit. Assoc.*, 1912, 200), Clerk ("Ganet Lecture," Junior Institution of Engineers, 1913), and Wheeler (this vol., p. 81). So far as we know, however, no figures have as yet been given for the effect of the velocity of a gas-mixture on the limits of its propagation of flame.

The methods used for moving the mixture and determining its velocity were those described under sub-ignition-temperature. Great care had to be taken in determining the upper limit for propagation against the gas-current, as the flame passed with great velocity down the 10 mm. bent glass tube joining the limit tube to the reservoir. This gave very little time for preventing the flame from getting into the reservoir. The results obtained are given in table XXI.

TABLE XXI.

*Showing the Effect of the Linear Velocity of an Ether-Air Mixture on its Downward Propagation of Flame Limits, as determined in a 5 cm. Glass Tube at  $20 \pm 2^\circ$ .*

Flame moving in the direction of gas current.

Velocity in cm. per sec.	Percentage of ether in mixture at lower limit.	Percentage of ether in mixture at upper limit.
0	2.13	6.15
1	1.97	6.40
3.5	1.95	6.50
9	1.95	6.65

Flame moving against the gas current.

0	2.13	6.15
1	—	6.25
3.5	—	6.25
9	—	6.25

It was found to be impossible to find the lower limit of propagation when the flame was moving against the stream, as it merely became a question of the velocity of the stream as compared with that of the flame in the mixture used. It will be seen from the upper portion of the table that the velocity of the gas-current affects very appreciably the percentage mixture which will propagate flame. That a portion of this change is due to turbulence caused in the gas, however, appears to be very likely, for, in the cases tried, when the flame moves against the gas-current with any real velocity, the upper limit is always the same.

The figures given for zero velocity in table XXI are those found with one cock closed in the ordinary manner. As conditions are slightly different when both cocks are open, it was decided to try such an experiment. The upper limit found under these conditions

was 6.30 per cent., but the convection due to the flame probably caused this figure to be a little high, on account of the air drawn into the tube during the passage of the flame. It almost appears as if, when a flame is travelling against a gas-stream, the turbulence due to the velocity of the stream practically balances the effect of that velocity in hindering the propagation of flame.

*Influence of the Presence of Glyceryl Trinitrate, Diethyl Peroxide, and Ethyl Hydrogen Peroxide.*

In the experiments to determine the effect of glyceryl trinitrate on the limits of propagation for ether-air mixtures, the mixture used was charged with glyceryl trinitrate, as described under the experiments on the determination of sub-ignition-temperatures. The results obtained when using ether-air mixtures containing diethyl peroxide and ethyl hydrogen peroxide are given in table XXII.

TABLE XXII.

*Showing the Effects on the Limits of Propagation of Flame of adding Amounts of Glyceryl Trinitrate, Diethyl Peroxide, and Ethyl Hydrogen Peroxide to Certain Ether-Air Mixtures.*

Direction of propagation.	Limit.	Mixture used (with air).	Percentage of ether in limit mixture.
Upwards .....	Lower	Ether.	1.93
Downwards ...	"	"	2.15
"	Upper	"	6.15
Upwards .....	Lower	Ether saturated with glyceryl trinitrate at 20°.	1.95
Downwards ...	Upper	"	6.15
"	Lower	Diethyl peroxide.	2.34
"	"	Ether containing 25 per cent. of diethyl peroxide by weight.	2.18
"	Upper	"	10.1
"	Lower	Ether containing 10 per cent. of 80 per cent. ethyl hydrogen peroxide by weight.	2.17
"	Upper	"	6.5

The peroxides of ether are calculated as ether in making up the percentage volume occupied by the solvent in the limiting mixture. It will be seen that glyceryl trinitrate appears to have no effect on either limit, and that the peroxides have little effect on the lower limit, but that they raise the upper limit very appreciably.

The glyceryl trinitrate did not appear to affect the flames given, but the flames, when peroxides were present, were invariably fiercer than when ether alone was used, except, perhaps, at the extreme limit.



## SECTION III.

*Investigation of Various Means of Ignition.*

A series of experiments was carried out in which sparks obtained by various means were used for attempting to ignite ether-alcohol-air mixtures. It was found that steel to steel, emery to steel, and pyrites to steel sparks appeared to be unable to cause the inflammation of any of the many mixtures tested. Ferro-cerium to steel sparks, however, ignited most mixtures very readily. The igniting powers of a small gas flame and a moderately powerful electric spark appeared to be of the same order, and both almost invariably gave rise to ordinary combustion, the limits of propagation of flame being naturally identical in the two cases. In the case of ether-alcohol-air mixtures, quick heating of a mixture, up to, but not far above, its sub-ignition-temperature, seemed to give rise to a cool flame which had limits for propagation varying from those of ordinary inflammation.

*The Cool Flame.*—The difference in propagation-limits for the two methods of combustion was particularly noticeable in the case of concentrated ether-air mixtures, as the flame travelled easily through a 20 per cent. mixture in a horizontal tube 4 cm. in diameter, although the upper limit for the propagation of ordinary combustion in a 5 cm. tube would be 8 per cent. No determinations of the limits for propagation of a cool flame were made, but experiments carried out for other purposes indicate that it is unlikely that such a flame could propagate downward through a mixture containing much more than 6 per cent. of ether. This flame was occasionally observed when electrical ignition was utilised, more particularly with high concentrations of ether or low pressures. It appeared, as stated by Perkin, to require very little oxygen, and the products of combustion were characteristic. It was found that the addition of less than 1 per cent. of oxygen to a mixture of 9 per cent. of ether in nitrogen was sufficient to give luminous combination below  $220^{\circ}$ . The increase of temperature caused by this flame in a mixture containing less than 3.5 per cent. of ether and heated to its sub-ignition-temperature was insufficient to be indicated by the fine thermo-couple registering the temperature of the gas in the ignition tube. The increase of pressure caused by it was also very small. This was measured roughly by its effect on a column of mercury so arranged that after ignition the mercury in both limbs of a U-tube would be level. The mean of three experiments with a 3.9 per cent. mixture gave a momentary

increase of pressure equal to 3 or 4 cm. Mixtures containing more ether gave far greater pressures.

It was found that a 0.3 cm. mesh iron gauze, or a 0.2 cm. mesh brass gauze, prevented the passage of a cool flame down a glass tube 7 cm. in diameter.

### *Discussion of Results.*

The sub-ignition-temperature figures given above agree fairly well with ignition-temperatures previously published for alcohol and acetone. The sub-ignition-temperature given for ether-air mixtures, however, whilst agreeing almost exactly with the ignition-temperature given by Alilaire, differs notably from the other figures available. The difference is probably to be accounted for by the fact that in the methods employed to obtain these, no account was taken of the cool flame of ether—the cool flame of alcohol can only be obtained near the temperature at which an explosion or ordinary combustion occurs directly. This may be justifiable and necessary in the determination of ignition-temperatures, but involves the neglect of a phenomenon which can, and very often does, give rise to ordinary combustion under suitable conditions. Moreover, these conditions are precisely those liable to obtain during solvent-recovery on the manufacturing scale, namely, the presence of a large volume of the solvent-air mixture and some degree of confinement.

That ordinary combustion of a dangerous nature could be caused by heating an ether-air mixture in glass tubes to  $187^{\circ}$  was proved again and again when using 4 and 5.5 cm. tubes, particularly if the percentage of solvent lay between 5 and 9. That this result was a genuine one was proved by stopping a current of ether in air flowing along a glass tube kept at  $187^{\circ}$ . Ignition of the ether occurred in every case. The method employed to determine sub-ignition-temperatures thus appears to be a practical one, and also has the advantage of being easily adaptable to determine the effect of substituting for glass any material that might be used in manufacture.

The ignition observed by Alilaire must indubitably have commenced as a cool flame. The temperatures necessary to obtain such a flame in mixtures containing fair quantities of ether, as shown by us, are fairly near the temperatures attainable in a steam-heated building, particularly when it is considered that the presence of metals lowers the sub-ignition-temperature appreciably. On the other hand, the results previously obtained for the ignition-

temperature of ether-air mixtures are far above those one can conceive of being attained in such a building, except in the most extraordinary circumstances.

The results show that a quiescent gas appears to be more easily ignited than one in motion, but the experimental work covers only a very small range of velocities, and in any case the propagation of flame is more easily and quickly carried out by gas in motion.

The presence of glyceryl trinitrate in a gas-mixture, as was anticipated from its amount, does not seem to affect the temperature of sub-ignition or the limits of propagation of flame. The peroxides sometimes present in ether in very small amounts can, however, affect both its ignition and its propagating qualities if present in sufficient quantity. Our work seems to indicate that their influence in causing primary ignition could only be inappreciable, although it is quite conceivable that they could well affect the change from cool to ordinary flame.

Reduction of pressure appeared to cause a lowering of the sub-ignition-temperature of the mixtures examined, but the effect of pressure alone within the range of variation of atmospheric pressure can scarcely have a practical influence on the ignition of the solvent-air mixtures, as for ether-air, for example, a reduction of pressure of 10 cm. near atmospheric pressure caused a variation in the sub-ignition-temperature of less than  $2^{\circ}$ .

The only phenomenon that could be expected to reduce the sub-ignition-temperature of ether-alcohol-air and ether-air mixtures below the danger limit is thus that described as shock ignition. With a difference of pressure of less than half an atmosphere, it was possible by this method to ignite a gas-mixture at least  $170^{\circ}$  below its sub-ignition-temperature, so that it is quite conceivable that the development of sudden differences of pressure on the manufacturing scale might easily be the determining factor in bringing about ignition of the solvent-laden air. Exactly how this is to be brought about can only be conjectured, as our inside knowledge of gas-ignition, particularly as regards this fresh phenomenon, is very limited. The present work has shown how many accidents could happen, but much remains to be done before any sound explanation can be given of such a conflagration as was described in *The Times* of March 28th, 1919, when a bottle of ether exploded in a military hospital at Southage. According to the same report, explosions of bottles of ether are of somewhat frequent occurrence.

The results given in the older work for the limits for propagation of flame in ether-air mixtures are 1.8 per cent. and about 9 per cent., the latter being apparently far out, whilst those for alcohol-air mixtures agree fairly well with our results, particularly

as regards the lower limit. The change from 5 cm. glass to 15 cm. iron tube affects the results for the upper limit for horizontal and upward propagation in ether-air mixtures very materially, the limits becoming well over 20 per cent. in each case, instead of 8 per cent. for horizontal propagation and 16 per cent. for upward propagation. The extreme limits determined for ether-air mixtures are thus 1.73 and 23.30 per cent. The upper limit for propagation in alcohol-air mixtures in 5 cm. glass tubes was found to be 18.95 at 60°. As this figure was well above the highest concentration of alcohol vapour obtainable during normal recovery, there was no point in repeating this in the 15 cm. iron tube. The lower limit of propagation for alcohol-air mixtures was only very slightly altered in the large iron tube, falling from 4.24 per cent. in the 5 cm. glass tube to 4.16 per cent.

The results for the propagation of flame in ether-alcohol-air mixtures obtained during this investigation are distinctly interesting. It is found that Le Chatelier's rule holds for all directions of propagation for the lower limit, and for the upper limit for downward propagation. The rule does not hold for the other two directions of propagation for the upper limit, the discrepancies being very considerable in the case of upward propagation. Wheeler's work on acetone-air mixtures has already been discussed, and it may suffice here to state that the limits given by him are 2.15 and 9.7 per cent., our results being 2.88 and 12.40 per cent. The lower limit of 5 per cent. given by Brunswig is obviously wrong, but the upper-limit figure of 12 per cent. is very near that found by us.

It will be seen that the effect of temperature and pressure on the limits for the propagation of flame in ether-air mixtures is quite material. The influence of the velocity of the gas-current was not examined throughout a sufficient range to enable sound conclusions to be drawn as to its effect under manufacturing conditions, but it is fairly clear that a margin must be allowed for this factor when dealing with the limit results obtained. The presence of 1 per cent. of the peroxides of ether in ether-air mixtures appears to have no appreciable effect on the lower limit for the propagation of flame, and it is by no means likely that there would be sufficient peroxide present under practical conditions to affect the upper limit materially.

#### *Summary.*

The soap-bubble method described by McDavid (*loc. cit.*) gave for the ignition-temperature of ether-air mixtures results varying from 859° to 1068°. The method seemed to be untrustworthy.

The other method used seemed to give the minimum temperature at which the reaction in a combustible gas-mixture became self-supporting—called the sub-ignition-temperature. This temperature, which appears to be the one required from a safety point of view, was  $187^{\circ}$  for ether-air mixtures in glass, and varied from  $187^{\circ}$  to about  $500^{\circ}$  for the different ether-alcohol-air mixtures used. It was about  $500^{\circ}$  for acetone-air mixtures. The presence of appreciable quantities of metal in the vessels used lowered the sub-ignition-temperature.

Decrease of pressure appeared to reduce the sub-ignition-temperature of a mixture, but the presence of small quantities of glyceryl trinitrate or of diethyl peroxide had little effect on the sub-ignition-temperature of ether-air mixtures. The sub-ignition-temperature of such mixtures was lowered by the presence of ethyl hydrogen peroxide. The effect of slight velocities seemed to be to raise the sub-ignition-temperature of ether-air mixtures.

When an exhausted vessel is quickly put into communication with a reservoir containing ether-air or carbon disulphide-air mixtures, under specified conditions the gas can be ignited at the ordinary temperature. This phenomenon has been termed shock ignition.

The limits for the propagation of flame in mixtures of ether-alcohol-air and ether-acetone-air have been determined in 2.5 and 5 cm. tubes of glass and in 5 and 15 cm. tubes of iron. The extreme limits found were 1.73 and 23.30 per cent. for ether-air mixtures, 4.16 and 18.95 per cent. for alcohol-air mixtures, and 2.88 and 12.40 per cent. for acetone-air mixtures. The upper limit for propagation in alcohol-air was determined at  $60^{\circ}$ . Figures obtained with the 15 cm. iron tube often differed appreciably from those obtained with 5 cm. glass tubes.

Le Chatelier's rule was found to hold fairly well for ether-alcohol-air mixtures, except for horizontal and upward propagation in the case of the upper limit. The only considerable deviation from the rule in the case of ether-acetone-air mixtures was observed for upward propagation and the upper limit.

Increase of temperature was found to raise the upper limit for propagation in ether-air notably, and reduction of pressure was found to narrow the limits. Increase in the velocity of the gas-mixture widened the limits materially. The presence of the peroxides of ether scarcely affected the lower limit of propagation in ether-air, but any considerable quantity raised the upper limit of such a mixture.

It was found impossible to ignite ether-alcohol-air mixtures by means of steel to steel, emery to steel, or pyrites to steel sparks, but

inflammation was readily obtained when using ferro-cerium to steel sparks.

Many of the properties of ether-air mixtures appear to be explained by the formation of a cool flame.

Further work is contemplated on the phenomenon referred to as shock ignition.

We desire to express our thanks to Messrs. Nobel's Explosives Co., Ltd., for whom the work was carried out, and particularly to Mr. W. Rintoul, Manager of the Research Section, for kind permission to publish our results. We also wish to thank Mr. A. W. Sanderson for assistance in carrying out some of the experimental work.

THE RESEARCH LABORATORIES,

ARDEER FACTORY, STEVENSTON. [Received, September 22nd, 1919.]

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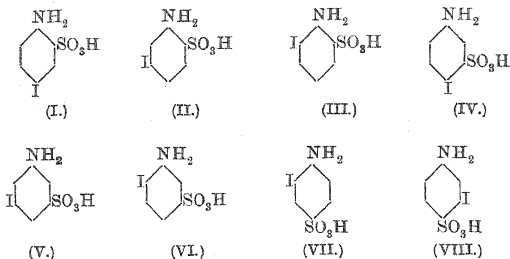
### CXXXIX.—*The Conductivities of Iodoanilinesulphonic Acids.*

By MARY BOYLE.

No systematic study of the halogen-substituted derivatives of the anilinesulphonic acids seems to have been attempted. Eight out of the ten possible monochloro-, about five of the monobromo-, and three moniodo-derivatives have been described by P. Fischer, Post, Meyer, Bahlmann, etc., but in some cases the constitution is left uncertain and in most others there is merely a simple statement of the preparation and properties of individuals; owing to the incomplete character of the group, no comparative study of either the chloro-, bromo-, and iodo-substituted derivatives or of the different members of a group of acids substituted by one particular halogen has been possible. It was thought that it might be interesting to study one particular property throughout a complete series, in order to determine how the value of that property is affected by the position in the nucleus taken by the halogen relative to the two other groups present. The series chosen was that of the iodoanilinesulphonic acids, and the property that of electrical conductivity.

So far, however, it has not been found possible to prepare the

ten possible isomerides, but the following eight, of established constitution, are now known:



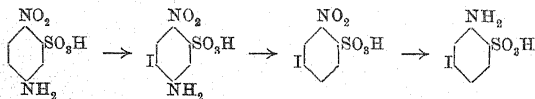
The series of chloroanilinesulphonic acids described by P. Fischer, Meyer, Claus, Goslich, Limpricht, etc., corresponds closely with the above, except that the chloro-analogue of III is unknown, and that a 3-chloroaniline-2-sulphonic acid described by Post and Meyer has no counterpart, up to the present, among the iodine compounds.

2-Iodoaniline-4-sulphonic acid (VII) was described in a patent by Kalle & Co. (D.R.-P. 129808), and its constitution established in 1909.

4-Iodoaniline-2-sulphonic acid (I) and 3-iodoaniline-4-sulphonic acid (VIII) were described by the author in 1909 (T., 95, 1689, 1709).

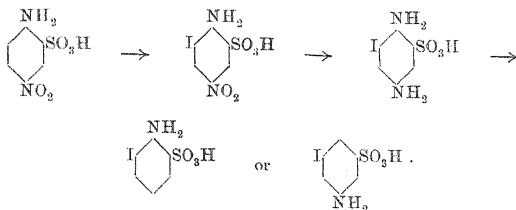
The others have been prepared from various nitroanilinesulphonic acids, as described below.

5-Iodoaniline-2-sulphonic acid (II) was obtained from *p*-nitroaniline-*m*-sulphonic acid by treating it with iodine chloride, removing the amino-group, and subsequently reducing the nitro-group.



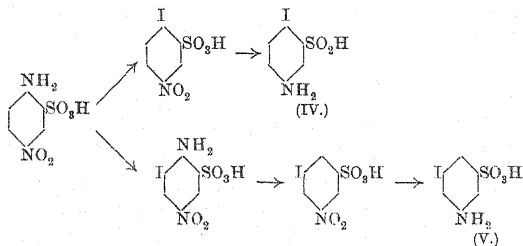
6-Iodoaniline-2-sulphonic acid (III) was prepared with more difficulty, and small quantities only have been obtained. The *p*-nitroaniline-*o*-sulphonic acid described in 1911 (T., 99, 325) gave, when treated with iodine chloride, an iodo-derivative, for which only one configuration is possible. Reduction of the nitro-group gave a diaminosulphonic acid, which, by the loss of one amino-

group, could yield two different iodoanilinesulphonic acids, as figured below:

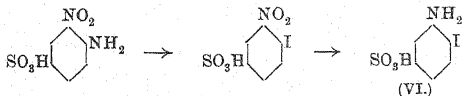


Considerations of steric hindrance would suggest the first as the more probable reaction, and that it does take place exclusively is proved by the conversion of the iodoanilinesulphonic acid into the well-known 2:3-di-iodobenzenesulphonic acid.

4-Iodoaniline-3-sulphonic acid (IV) and 5-iodoaniline-3-sulphonic acid (V) were both obtained from *p*-nitroaniline-*o*-sulphonic acid by submitting it to the following series of reactions:



6-Iodoaniline-3-sulphonic acid (VI) was obtained by a similar series of reactions from *o*-nitroaniline-*p*-sulphonic acid.



These acids resemble each other in appearance, being well characterised, colourless substances crystallising from water in needles. They vary somewhat in solubility in water, the 6-iodo-

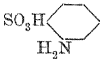
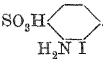
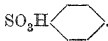


aniline-2-sulphonic acid being readily soluble, most of the others giving  $N/32$ — $N/64$ -solutions, and 3-iodoaniline-4-sulphonic acid dissolving sparingly. The latter acid crystallises with one molecule of water; the rest are anhydrous.

In the experiments on conductivities, the main difficulty experienced was in the accurate determination of the strength of the acid solution. The unsubstituted anilinesulphonic acids were first investigated, the pure acids being either (1) weighed out to the required strength, or (2) titrated with standard alkali and diluted to the required strength; the two methods were found to give identical results when special precautions in the standardisation of materials were taken. The numbers obtained in the case of the three anilinesulphonic acids are all higher than the corresponding numbers obtained by Ostwald (*Zeitsch. physikal. Chem.*, 1889, **3**, 106), Winkelblech (*ibid.*, 1901, **36**, 546), White and Jones (*Amer. Chem. J.*, 1909, **42**, 520), and Wheeler and Jones (*ibid.*, 1910, **44**, 159). It is to be noted, however, that these higher values give a better dissociation constant than do the earlier and lower ones. For example, for aniline-*p*-sulphonic acid, Ostwald gives a mean  $K=5.81 \times 10^{-4}$ , showing a maximum variation of  $0.8 \times 10^{-5}$ , Winkelblech a mean  $K=6.2 \times 10^{-4}$  with a variation of  $2.3 \times 10^{-5}$ , Wheeler and Jones a mean  $K=6.55 \times 10^{-4}$  and variation  $1.7 \times 10^{-5}$ , and the author a mean  $K=7.05 \times 10^{-4}$  with a variation of  $0.6 \times 10^{-5}$ .

For aniline-*o*-sulphonic acid, the mean value  $K=4.29 \times 10^{-3}$ , as against Ostwald's  $K=3.21 \times 10^{-3}$ , and for aniline-*m*-sulphonic acid the value  $K=2.11 \times 10^{-4}$ , as against Ostwald's  $K=1.85 \times 10^{-4}$  and Wheeler and Jones'  $K=1.97 \times 10^{-4}$ , have been obtained.

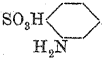
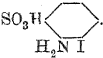
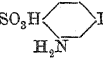
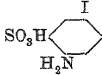
The introduction of iodine into the nucleus increases the conductivities of the acids very considerably, bringing them into the category of strong acids, which do not obey Ostwald's dilution law; in the case of some of the aniline-*m*-sulphonic acids only can a value of  $K$  which is even approximately constant be obtained. It is the position of the iodine relative to the amino-group which is the determining factor; whether in the meta- or para-position the effect in increasing the strength of the acid is approximately the same, but when in the ortho-position the effect is very marked. The influence of the amino-group in diminishing the strength of the sulphonic acid is almost entirely neutralised by the ortho-substituted iodine, and the iodoamino-sulphonic acid is found to conduct to the same extent as benzenesulphonic acid itself. A comparison of 6-iodoaniline-2-sulphonic acid with aniline-*o*-sulphonic acid and with benzenesulphonic acid shows this clearly.

			
$\nu$ .	$\lambda_{\nu}$ .	$\lambda_{\nu}$ .	$\lambda_{\nu}$ .
32	109.5	—	321.07
64	144.1	340.0	—
128	183.4	348.2	350.47
256	225.8	353.1	—
512	265.0	356.7	356.38
1024	299.5	357.8	359.03
2048	—	—	354.22

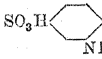
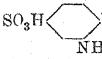
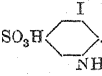
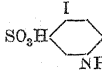
The figures for benzenesulphonic acid are those given by Wightman and Jones (*Amer. Chem. J.*, 1911, **46**, 56).

The three following tables give the conductivities of the iodo-substituted acids side by side with those of the unsubstituted acid from which they are derived.

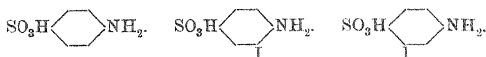
*Aniline-o-sulphonic Acid,*

				
$\nu$ .	$\lambda_{\nu}$ .	$\lambda_{\nu}$ .	$\lambda_{\nu}$ .	$\lambda_{\nu}$ .
32	109.5	—	—	—
64	144.1	340.0	—	—
128	183.4	348.2	309.5	289.6
256	225.8	353.1	333.2	320.9
512	265.0	356.7	348.7	341.6
1024	299.5	357.8	357.4	355.0

*Aniline-m-sulphonic Acid,*

						
$\nu$ .	$\lambda_{\nu}$ .	$\lambda_{\nu}$ .	$\lambda_{\nu}$ .	$K \times 10^4$ .	$\lambda_{\nu}$ .	$K \times 10^4$ .
32	28.15	—	—	—	—	—
64	39.12	242.3	115.3	23.5	73.98	8.30
128	54.01	286.4	149.5	23.0	99.14	8.15
256	73.98	319.3	191.2	23.5	130.2	8.02
512	99.28	342.2	235.5	24.1	167.8	7.94
1024	131.5	358.2	279.9	—	210.4	8.00
	$K =$		$K =$		$K =$	
	$2.11 \times 10^{-4}$ .		$23.5 \times 10^{-4}$ .		$8.08 \times 10^{-4}$ .	

Ostwald's value  $\lambda_{\infty} = 356$  has been used in calculating the dissociation constants of the anilinesulphonic acids, and  $\lambda_{\infty} = 360$  for calculating those of the iodoanilinesulphonic acids.

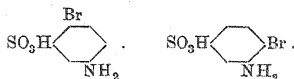
*Aniline-p-sulphonic Acid.*

$\nu$ .	$\lambda_{\mu}$	$\lambda_{\mu}$	$\lambda_{\mu}$
32	49.73	266.7	—
64	68.30	301.9	—
128	92.54	329.5	—
256	122.9	347.4	228.7
512	159.4	360.0	268.4
1024	200.7	366.2	302.7

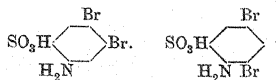
The same screening of the amino-group is brought about by other groups than iodine, for example, bromine, the nitro-group, hydroxy-group, etc., although none is quite so effective as iodine. From the literature on the subject of conductivities of acids, the following data have been selected as bearing out what has been shown to be true of iodo-substituted acids.

*Bromo-derivatives of Anilinesulphonic Acids.*

The acid containing bromine in the ortho-position with respect to the amino-group has a greater conductivity at all dilutions than the one with bromine in the para-position.

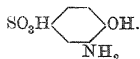
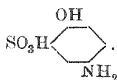


$\nu$ .	$\lambda_{\mu}$	$\lambda_{\mu}$
64.0	70.0	—
73.5	—	224.4
128.0	92.3	—
147.0	—	351.8
256.0	122.5	—
294.0	—	276.5
512.0	157.4	—
588.0	—	296.3
1024.0	197.5	—
1176.0	—	312.6



$\nu$ .	$\lambda_{\mu}$	$\lambda_{\mu}$
109.8	—	338
219.6	—	343
278.0	338	—
439.2	—	346
556.0	346	—
878.4	—	348
1112.0	351	—

*Hydroxy-derivatives of Anilinesulphonic Acids.*

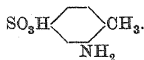
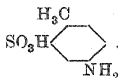


$\nu$ .	$\lambda_{\nu}$ .	$\lambda_{\nu}$ .
64	—	26.5
128	—	36.9
256	16.0	51.0
512	22.4	69.8
1024	31.3	125.0

Here the same thing is observed, although both acids have a smaller conductivity than the unsubstituted metanilic acid.

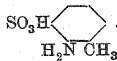
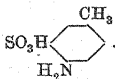
*Alkyl Derivatives of Anilinesulphonic Acids.*

The introduction of methyl into aniline-*m*-sulphonic acid gives results in harmony with the above.



$\nu$ .	$\lambda_{\nu}$ .	$\lambda_{\nu}$ .
32	12.6	—
64	17.7	42.3
128	24.7	56.8
256	34.5	77.2
512	47.7	104.6
1024	—	137.5

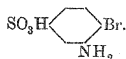
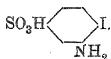
In the case of aniline-*o*-sulphonic acid, however, the position of the substituted group in the nucleus seems to make practically no difference to the conductivity value.



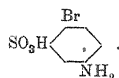
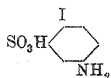
$\nu$ .	$\lambda_{\nu}$ .	$\lambda_{\nu}$ .
32	53.9	51.0
64	73.7	69.9
128	99.5	94.6
256	131.4	125.2
512	169.1	162.5
1024	210.9	—

*Halogen Derivatives of Anilinesulphonic Acids.*

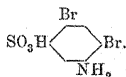
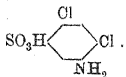
Iodine is more effective than bromine in neutralising the effect of the amino-group, and bromine than chlorine. This is seen from a consideration of the three following tables:



$v.$	$\lambda_{90}$	$\lambda_{90}$
64.0	243.3	—
73.5	—	224.4
128.0	286.4	—
147.0	—	[251.8
256.0	319.3	—
294.0	—	276.5
512.0	342.2	—
588.0	—	296.3
1024.0	358.2	—
1176.0	—	312.6



$v.$	$\lambda_{90}$	$\lambda_{90}$
64.0	73.98	70.0
128.0	99.14	92.3
256.0	130.2	122.5
512.0	167.8	157.4
1024.0	210.4	197.5



$v.$	$\lambda_{90}$	$\lambda_{90}$
64.0	—	—
71.9	—	262
128.0	130.0	—
143.8	—	289
256.0	158.4	—
287.6	—	313
512.0	189.2	—
575.2	—	329
1024.0	227.9	—
1150.0	—	340
2048.0	268.5	—

EXPERIMENTAL.

*Preparation of the Acids.*

4-Iodoaniline-2-sulphonic acid was prepared from aniline-*o*-sulphonic acid according to the method previously described (T., 1909, **95**, 1698). After repeated crystallisations, the acid still possessed a faint violet tinge (Found: C=24.03; H=1.99. Calc.: C=24.07; H=2.00 per cent.).

*Solubility.*—One hundred grams of water dissolve 0.51 gram of the acid at 25°.

*5-Iodoaniline-2-sulphonic Acid.*—The method of preparation consists in (a) introducing iodine into *p*-nitroaniline-*m*-sulphonic acid, (b) displacing the amino-group by hydrogen, (c) reducing the nitro-group.

(a) *Preparation of 6-Iodo-4-nitroaniline-2-sulphonic Acid.*—Fifteen grams of 4-nitroaniline-3-sulphonic acid, prepared by Eger's method from aniline-*m*-sulphonic acid (Ber., 1888, **21**, 2581), were dissolved in a large volume of boiling water, a little hydrochloric acid was added, and 11.2 grams of iodine chloride were then passed into the solution, which was kept at 90—95°. Experiments were carried out at lower temperatures, but the sparing solubility of the acid enabled only small quantities to be worked up at a time, and the yield was only inappreciably increased. The reddish-yellow solution, after remaining for half an hour, was evaporated to a very small bulk, when the dark yellow acid separated on cooling. A yield of 20.4 grams, amounting to 87 per cent. of the theoretical, was obtained.

(b) *Preparation of 4-Iodo-2-nitrobenzenesulphonic Acid.*—Fifteen grams of the above acid were diazotised in sulphuric acid solution by means of 3 grams of sodium nitrite. The sparingly soluble diazo-compound was then boiled with alcohol under a reflux condenser, and the dark-coloured residue, after removing the alcohol, was dissolved in water, neutralised with sodium carbonate and boiled with animal charcoal; the yellow filtrate deposited, on concentration, long, yellow needles, which became opaque on exposure to air. The yield amounted to nearly 70 per cent. of the theoretical.

(c) *Preparation of 5-Iodoaniline-2-sulphonic Acid.*—The nitro-acid was reduced, as usual, with stannous chloride at 100°. There was little apparent action, the solution retaining its yellow colour, but when the yellow solid which was precipitated on cooling was dissolved in sodium carbonate, a white amino-acid was obtained

from this solution by adding concentrated acid. Proof of its structure was obtained by replacing the amino-group by iodine and converting the di-iodobenzenesulphonic acid into a chloride melting at  $75^{\circ}$ , and identical with 2:4-di-iodobenzenesulphonyl chloride:

0.1341 gave 0.1181  $\text{CO}_2$  and 0.0248  $\text{H}_2\text{O}$ .  $\text{C}=24.01$ ;  $\text{H}=2.05$ .

$\text{C}_6\text{H}_6\text{O}_3\text{NIS}$  requires  $\text{C}=24.07$ ;  $\text{H}=2.00$  per cent.

*Solubility.*—One hundred grams of water contain 0.26 gram of acid at  $25^{\circ}$ .

*6-Iodoaniline-2-sulphonic Acid.*—6-Iodo-4-nitroaniline-2-sulphonic acid (T., 1911, **99**, 330) was reduced with stannous chloride at  $100^{\circ}$  to 6-iodo-*p*-phenylenediamine-2-sulphonic acid, which is a white, crystalline substance sparingly soluble in water. A small quantity (2.5 grams) was diazotised in the minimum amount of sulphuric acid by adding 0.55 gram of sodium nitrite (theoretical amount for one amino-group is 0.53 gram); the dark yellow diazo-compound was then collected and boiled with alcohol. After evaporating off the alcohol and boiling the neutralised residue with animal charcoal, the filtered solution and the amino-acid precipitated from it were still somewhat coloured. This amino-acid has not yet been obtained in a colourless condition; it crystallises in pale brown needles from water, in which it is rather readily soluble. Its conversion into 2:3-di-iodobenzenesulphonyl chloride, melting at  $127^{\circ}$ , confirmed its constitution:

0.1937 gave 0.1701  $\text{CO}_2$  and 0.0370  $\text{H}_2\text{O}$ .  $\text{C}=23.95$ ;  $\text{H}=2.11$ .

$\text{C}_6\text{H}_6\text{O}_3\text{NIS}$  requires  $\text{C}=24.07$ ;  $\text{H}=2.00$  per cent.

*4-Iodoaniline-3-sulphonic Acid.*—Nineteen grams of *p*-nitroaniline-*o*-sulphonic acid (T., 1911, **99**, 324) were diazotised in sulphuric acid solution by 5.7 grams of sodium nitrite, and the bright yellow diazo-compound was decomposed by potassium iodide. A voluminous yellow precipitate of potassium 2-iodo-5-nitrobenzenesulphonate separated at once from the hot solution, and was collected and well washed with cold water. This salt was suspended in concentrated hydrochloric acid and reduced with stannous chloride, the completion of the reduction being readily ascertained by the change in colour and in the appearance of the crystalline product. The amino-acid was purified, as usual, by precipitating it with concentrated acid from its solution in sodium carbonate. It separates from a concentrated aqueous solution in small, sparkling crystals, from more dilute solutions in fine, transparent needles. Its conversion into 2:5-di-iodobenzenesulphonyl chloride, melting at  $132^{\circ}$ , afforded proof of its constitution:

0.1871 gave 0.1644  $\text{CO}_2$  and 0.0331  $\text{H}_2\text{O}$ .  $\text{C}=23.96$ ;  $\text{H}=1.97$ .

$\text{C}_6\text{H}_4\text{O}_3\text{NIS}$  requires  $\text{C}=24.07$ ;  $\text{H}=2.00$  per cent.

*Solubility*.—One hundred grams of water contain 1.36 grams of anhydrous acid at  $25^\circ$ .

5-Iodoaniline-3-sulphonic acid was prepared from *p*-nitroaniline-*o*-sulphonic acid through 6-iodo-4-nitroaniline-2-sulphonic acid by (1) removing the amino-group, (2) reducing the nitro-group. When the diazo-compound was boiled with alcohol, nitrogen was evolved rapidly, and, after about forty-five minutes, a clear, pale yellow solution was obtained, from which, on concentration, pale yellow crystals separated; these were neutralised with sodium carbonate, and the sodium salt was recrystallised. Sodium 3-iodo-5-nitrobenzenesulphonate was dissolved in hydrochloric acid and reduced with stannous chloride at  $100^\circ$ ; precipitation of the amino-acid as a cream-coloured, crystalline mass followed almost immediately. The acid, dissolved in alkali and reprecipitated by mineral acid, was then repeatedly crystallised from hot water, separating in fine, white needles:

0.1778 gave 0.1569  $\text{CO}_2$  and 0.0326  $\text{H}_2\text{O}$ .  $\text{C}=24.07$ ;  $\text{H}=2.03$ .

$\text{C}_6\text{H}_4\text{O}_3\text{NIS}$  requires  $\text{C}=24.07$ ;  $\text{H}=2.00$  per cent.

*Solubility*.—One hundred grams of water dissolve 1.31 grams of anhydrous acid at  $25^\circ$ .

The constitution of the acid was established by replacing the amino-group by iodine and converting the resulting di-iodobenzene-sulphonic acid into 3:5-di-iodobenzenesulphonyl chloride, which crystallised from ether in needles melting at  $93^\circ$ .

6-Iodoaniline-3-sulphonic Acid.—*o*-Nitroaniline-*p*-sulphonic acid was prepared (1) by nitrating sulphanilic acid according to Nietzki's method (*Ber.*, 1885, **18**, 294), (2) by sulphonating *o*-nitroaniline by Hardtung's method (*Annalen*, 1881, **206**, 96). After displacing the amino-group by iodine, and subsequently reducing the nitro-group, the iodoaminosulphonic acid was obtained as a grey powder, which crystallised from a large bulk of water:

0.2075 gave 0.1833  $\text{CO}_2$  and 0.0388  $\text{H}_2\text{O}$ .  $\text{C}=24.09$ ;  $\text{H}=2.07$ .

$\text{C}_6\text{H}_4\text{O}_3\text{NIS}$  requires  $\text{C}=24.07$ ;  $\text{H}=2.00$  per cent.

*Solubility*.—One hundred grams of water contain 0.48 gram of acid at  $25^\circ$ .

2-Iodoaniline-4-sulphonic acid was prepared as previously described (T., 1909, **95**, 1693) (Found:  $\text{C}=24.03$ ;  $\text{H}=2.11$ . Calc.:  $\text{C}=24.07$ ;  $\text{H}=2.00$  per cent.).



*Solubility.*—One hundred grams of water dissolve 2.07 grams of the anhydrous acid at 25°.

3-Iodoaniline-4-sulphonic acid was prepared by reducing 2-iodo-4-nitrobenzenesulphonic acid (T., 1909, 95, 1708) by means of stannous chloride. The reduction proceeded rapidly on the water-bath, and was complete in less than an hour. The iodoamino-acid, precipitated from its solution in alkali by concentrated mineral acid, was recrystallised from water several times, separating in fine, transparent needles containing one molecule of water of crystallisation:

0.1861 gave 0.1552 CO<sub>2</sub> and 0.0425 H<sub>2</sub>O. C=22.74; H=2.53.

C<sub>6</sub>H<sub>4</sub>O<sub>3</sub>NIS, H<sub>2</sub>O requires C=22.71; H=2.52 per cent.

*Solubility.*—One hundred grams of water dissolve 0.194 gram of anhydrous acid at 25°.

Conductivity experiments were carried out in Ostwald cells in a thermostat at 25°. An ordinary Wheatstone bridge, carefully calibrated, and standard resistances were employed. The conductivity water was obtained by distilling first with acid, then with alkaline permanganate, finally alone, in the ordinary form of apparatus, consisting of tin distilling flask, block-tin condenser, and Jena-glass receiver. In making the solution of the acid for conductivity measurements, excess of the acid was shaken vigorously in a Jena-glass flask with conductivity water and allowed to remain for some time. The solid was then filtered off and the filtrate titrated against standard sodium hydroxide of slightly less strength; the solution was then diluted to that strength. Standard flasks, pipettes, and burettes were used throughout.

In the preparation of the standard solutions, conductivity water was used throughout. *N*/10-Sodium hydroxide was titrated against *N*/10-hydrochloric acid which had previously been standardised by means of pure sodium carbonate, and each solution was then diluted to *N*/32, *N*/64, *N*/128, *N*/256, and titrations of one against the other were carried out in order that errors introduced by the hydrolysis of the indicator, phenolphthalein, at such considerable dilutions should be obviated. The results of experiments carried out under these conditions agreed well with those obtained by weighing out the acid directly and dissolving it in the requisite amount of water. After one set of results had been obtained, the acid was recrystallised and the conductivity again determined; the recrystallisations and subsequent determination of conductivity were repeated until consecutive experiments gave identical results; in this way, the purity of the acid was guaranteed. In some cases,

ten crystallisations had to be carried through before satisfactorily concordant results were obtained.

Further experiments on the conductivities of the anilinesulphonic acids are being carried out, and it is hoped that the results may shortly be ready for publication.

I wish to express my thanks to Miss E. E. Field for valuable help given during the course of this investigation.

ROYAL HOLLOWAY COLLEGE,  
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[Received, October 8th, 1919.]



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**Terpene derivatives**, rotatory dispersion of (LOWRY and ABRAM), 300.

**Thioamides**, action of, with cupric and mercuric chlorides (RAY), 876.

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**Stannous**, chloride, reaction between arsenious chloride and (DURRANT), 134.

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**Tropic acid**,  $C_9H_{10}O_3$ .

*Tsuga canadensis* (hemlock), tannin of (MANNING and NIERENSTEIN), 662.

**Tauginic acid**, bromo-,  $C_8H_7O_4Br$ .

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## W.

**Water**, effect of electrolytes on the temperature of maximum density of (WRIGHT), 119.

**Sea water**, effect of sea-salt on the pressure of carbon dioxide and alkalinity in (PRIDEAUX), 1223.

**Weights**, molecular, determination of, by measurement of vapour pressure lowering (WRIGHT), 1165.

## FORMULA INDEX.

THE following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus  $C_1$  group,  $C_2$  group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Salts are placed with the compounds from which they are derived. The chlorides, bromides, iodides, and cyanides of quaternary ammonium bases, however, are registered as group-substances.

### $C_1$ Group.

$CH_4$  Methane, equilibrium in the system: carbon, hydrogen and (COWARD and WILSON), 1380.

$CO$  Carbon monoxide, combustion of, in hydrogen (RIDEAL), 993.

$CO_2$  Carbon dioxide, pressure of, in sea water (PRIDEAUX), 1223.

#### 1 II

$CHN$  Hydrocyanic acid, catalytic reduction of (BARRATT and TITLEY), 902.

$CH_2N_2$  Diazomethane, interaction of, with carbamide and thiocarbamide (WERNER), 1168.

$CH_3N$  Methylamine, preparation of, from chloropicrin (FRANKLAND, CHALLENGER, and NICHOLLS), 159.

#### 1 III

$CH_3ON_2$  Carbamide, decomposition of, in presence of nitric acid (PRICE), 1354; interaction of, with diazomethane and diazoethane (WERNER), 1168.

$CH_3N_2S$  Thiocarbamide, interaction of, with diazomethane and diazoethane, and its oxidation with potassium permanganate (WERNER), 1168.

$CO_2NCl_2$  Chloropicrin (GARDNER and FOX), 1188; reduction of (FRANKLAND, CHALLENGER, and NICHOLLS), 159.

### $C_2$ Group.

$C_2H_2$  Acetylene, propagation of flame in mixtures of air and (MASON and WHEELER), 578; action of mercuric chloride with (CHAPMAN and JENKINS), 847.

$C_2H_6$  Ethane, ignition of mixtures of air and (WHEELER), 81.

#### 2 II

$C_2H_2O_4$  Oxalic acid, double salts of, with the alkali metals (RIVETT and O'CONNOR), 1346.

$C_2H_4O_2$  Acetic acid, vapour pressure and dissociation of, in solution (McBAIN and KAM), 1332; lead sub-salt (DENHAM), 109; silver salt, solubility of, in acetic acid (KNOX and WILL), 853.

$C_2H_5N_2$  Diazoethane, interaction of, with carbamide and thiocarbamide (WERNER), 1168.

$C_2H_5O$  Ethyl alcohol, ignition of mixtures of ether, air and (WHITE and PRICE), 1462.

2 III

$C_2H_5O_2N_3$  Nitrosomethylurea, preparation and properties of (WERNER), 1095.

**C<sub>3</sub> Group.**

$C_3H_5N_3$  2-Aminoglyoxaline, and its salts (FARGHER and PYMAN), 246.

$C_3H_6O$  Acetone, vapour pressure and density of mixtures of methyl ethyl ketone and (PRICE), 1116; ignition of mixtures of air and (WHITE and PRICE), 1462.

$C_3H_6O_2$  Methyl acetate, rate of hydrolysis of, by hydrochloric acid (BURROWS), 1230.

Propionic acid, silver salt, solubility of, in propionic acid (KNOX and WILL), 853.

$C_3H_7N_2$  Substance, from oxidation of thiocarbamide with permanganate (WERNER), 1173.

$C_3H_5O_3$  Glycerol, and its nitric esters, absorption spectra of (HEPWORTH), 840.

3 III

$C_3H_4ON_2$  Cyanoacetamide, condensation of ketones with (KON and THORPE), 686.

$C_3H_8N_2S$  Ethylisothiocarbamide, and its picrate (WERNER), 1172.

**C<sub>4</sub> Group.**

$C_4H_8$   $\beta$ -Butylene, preparation of (KING), 1406.

4 II

$C_4H_6O_6$  Tartaric acid, rotation dispersion of alkyl esters of (FRANKLAND and GARNER), 636.

$C_4H_6N_2$  2-Methylglyoxaline, and its salts (FARGHER and PYMAN), 231.

$C_4H_8O$  Methyl ethyl ketone, preparation of, from *n*-butyl alcohol (KING), 1404; vapour pressure and density of mixtures of acetone and (PRICE), 1116.

$C_4H_{10}O$  *n*-Butyl alcohol, pure, preparation of, and the detection of impurity in it (ORTON and JONES), 1194.

Ethyl ether, ignition of mixtures of alcohol, air and (WHITE and PRICE), 1462.

$C_4H_{10}S$  Ethyl sulphide, reactions of, with mercuric iodide and alkyl iodides (RAY and GUHA), 1154.

$C_4H_{11}N$  Butylamine, preparation of (WERNER), 1010.

4 III

$C_4H_6O_2N_3$  Nitromethylglyoxalines (FARGHER and PYMAN), 234.

$C_4H_7ON_3$  Alacreatine, preparation of, and its salts (FARGHER and PYMAN), 253.

$C_4H_8O_7N_2$  Glyceryl methyl ether dinitrate (JONES), 76.

4 IV

$C_4H_4NCIS$  2-Chloro-4-methylthiazole (TCHERNIAC), 1072.

$C_4H_4ONS$   $\alpha$ -,  $\beta$ -, and *iso*-Methylrhodim (TCHERNIAC), 1075.

Thiocyanoacetone, and its isomerides (TCHERNIAC), 1071.

**C<sub>5</sub> Group.**

$C_5H_8N_2$  4:5-Dimethylglyoxaline, and its hydrochloride (FARGHER and PYMAN), 233.

$C_5H_{10}N_2$  Diazoisopentane (WERNER), 1101.

$C_5H_{12}O$  Amyl alcohol, use of, as a membrane (DONNAN and GARNER), 1313.

5 III

$C_5H_6O_4N_2$  Glyoxaline-4:5-dicarboxylic acid, preparation of, and its sodium salt (FARGHER and PYMAN), 227.

$C_5H_8O_4N_3$  2-Aminoglyoxaline-4:5-dicarboxylic acid (FARGHER and PYMAN), 259.



$C_5H_5O_2N_2$  2-Methylglyoxaline-4-carboxylic acid, and its salts (FARGHER and PYMAN), 230.

$C_5H_7ON_3$  2-Acetylaminoglyoxaline (FARGHER and PYMAN), 248.

$C_5H_7O_2N$  Ethyl cyanoacetate, condensation of ketones with (KON and THORPE), 686.

$C_5H_{11}O_2N_3$  Nitroso-*n*-butylurea (WERNER), 1101.

$C_5H_{12}ON_2$  *n*-Butylurea (WERNER), 1101.

## 5 IV

$C_5H_5ON_6Fe$  Nitroprussic acid, alkali and methylammonium salts (BURROWS and TURNER), 1429.

$C_5H_5ON_2Cl$  Glyoxaline-4-acetyl chloride, hydrochloride of (FARGHER and PYMAN), 1019.

$C_5H_7ONS$  Dimethylrhodim (TCHERNIAC), 1076.

**C<sub>6</sub> Group.**

$C_6H_4O_4$  Substance, from acetic anhydride and aconitic acid (TAYLOR), 889.

$C_6H_4O_6$  Aconitic acid, presence of, in sugar-cane juices, and its detection (TAYLOR), 886.

$C_6H_8S_2$  2:5-Dimethylthien (TCHERNIAC), 1085.

$C_6H_{10}N_2$  2:4:5-Trimethylglyoxaline, and its picrate (FARGHER and PYMAN), 233.

## 6 III

$C_6H_4N_6Fe$  Ferrocyanic acid, copper salt, use of, as a membrane (DONNAN and GARNER), 1313.

$C_6H_5ClS$  *p*-Chlorophenyl mercaptan, reaction of, with mercuric nitrite (RAY and GUHA), 1154.

$C_6H_6O_3Se$  Phenylselenious acid, preparation of, and its sodium salt (PYMAN), 167.

$C_6H_6O_3Se$  Phenylselenenic acid, and its salts (PYMAN), 169.

$C_6H_8O_2N_2$  2-Ethylglyoxaline-4-carboxylic acid, and its picrate (FARGHER and PYMAN), 1017.

$C_6H_{11}O_3N$  4-Hydroxyhygric acid (GOODSON and CLEWER), 926.

$C_6H_{12}ON$  Diacetoneamine, preparation and reactions of (EVEREST), 538.

$C_6H_{13}O_2N_3$  Nitrosoisomethylurea (WERNER), 1101.

## 6 IV

$C_6H_5O_3NSe$  *m*-Nitrophenylselenious acid (PYMAN), 169.

$C_6H_5O_3NSe$  *m*-Nitrophenylselenenic acid, and its salts (PYMAN), 170.

$C_6H_7O_3NSe$  *m*-Aminophenylselenenic acid, and its sodium salt (PYMAN), 175.

## 6 V

$C_6H_6O_5NIS$  Iodoanilinesulphonic acids, conductivity of (BOYLE), 1505.

**C<sub>7</sub> Group.**

$C_7H_8$  Toluene, determination of purity of (ORTON and JONES), 1055; commercial, estimation of the purity of (LUMSDEN), 1366.

## 7 II

$C_7H_7N$  Methylaniline, preparation of (FRANKLAND, CHALLENGER, and NICHOLLS), 198.

$C_7H_7S$  *p*-Tolyl mercaptan, reaction of, with mercuric nitrite (RAY and GUHA), 1152.

$C_7H_{12}O_2$  *cyclo*Hexanecarboxylic acid, preparation of (INGOLD and THORPE), 376.

7 III

$C_7H_{10}O_2N_2$  Ethyl 2-methylglyoxaline-4-carboxylate (FARGHER and PYMAN), 1017.

$C_7H_{13}O_3N$  Betonicine, and its salts (GOODSON and CLEWER), 932.  
Turicine, and its salts (GOODSON and CLEWER), 931.

7 IV

$C_7H_6O_3NAS$  1:2-Dihydrobenzoxazolone-4-arsinic acid (FARGHER), 991.

$C_7H_6O_3N_2AS$  5-Nitro-6-amino-*m*-tolylarsinic acid (FARGHER), 989.

$C_7H_7O_3N_2AS$  1:3-Benzodiazolearsinic acids (BAXTER and FARGHER), 1372.

$C_7H_8O_3N_2AS$  7-Methyl-1:2:3-benzotriazole-5-arsinic acid (BAXTER and FARGHER), 1378.

$C_7H_{11}O_3N_2AS$  5:6-Diamino-*m*-tolylarsinic acid (BAXTER and FARGHER), 1377.

**C<sub>8</sub> Group.**

$C_8H_{12}O_4$  *cyclo*Hexane-1:1-dicarboxylic acid (INGOLD and THORPE), 376.

$C_8H_{12}O_6$   $\gamma$ -Methylbutane- $\alpha\beta\delta$ -tricarboxylic acid, preparation of (THORPE), 684.

$C_8H_{16}O_5$  Dimethyl methylarabinside (IRVINE and DICK), 599.

$C_8H_{19}N$  *n*-Dibutylamine, preparation of (WERNER), 1010.

8 III

$C_8H_7O_2Br$  Bromotsuginic acid (MANNING and NIKRENSTEIN), 664.

$C_8H_9O_2N_3$  Nitrosobenzylurea (WERNER), 1101.

$C_8H_9N_3S_2$  Dithiazylamine, and its hydrochloride (TCHERNIAO), 1082.

$C_8H_{10}ON_2$   $\alpha$ -Cyano- $\Delta^1$ -*cyclopentene*acetamide (KON and THORPE), 697.

$C_8H_{12}O_2N_2$  Ethyl 2-ethylglyoxaline-4-carboxylate (FARGHER and PYMAN), 1018.

$C_8H_{12}O_3N_2$  Ethyl  $\alpha$ -hydroxy- $\beta$ -glyoxaline-4-propionate (FARGHER and PYMAN), 1020.

$C_8H_{13}O_2N$  Oscine, and its salts, resolution of (KING), 476.

$C_8ON_2S_3$  Substance, from chloropicrin and the potassium salt of 2:5-dithiol-1:3:4-thiodiazole (RAY, GUHA, and DAS), 1312.

8 IV

$C_8H_9O_3NSe$  *m*-Acetylaminophenylselenious acid, and its sodium salt (PYMAN), 173.

$C_8H_9O_3N_2AS$  Methyl-1:3-benzodiazole-5-arsinic acids (BAXTER and FARGHER), 1377.

$C_8H_9O_4NSe$  *m*-Acetylaminophenylselenic acid, salts of (PYMAN), 174.

**C<sub>9</sub> Group.**

$C_9H_8O_2$  Atropic acid, preparation of (MCKENZIE and WOOD), 834.

Cinnamic acid, molecular refractivity of derivatives of (WALKER and JAMES), 1243.

$C_9H_8N_2$  2-Phenylglyoxaline, preparation of, and its salts (FARGHER and PYMAN), 232.

$C_9H_8N_4$  Benzeneazoglyoxaline (FARGHER and PYMAN), 237.

$C_9H_{10}O_3$  Atrolactic acid, preparation of (MCKENZIE and WOOD), 833.

$\omega$ -Hydroxy-*m*-tolylacetic acid (GOUGH and THORPE), 1162.

Tropic acid, and its salts, resolution of (KING), 476.

Tropic acids, preparation of (MCKENZIE and WOOD), 828.

$C_9H_{10}N_4$  2-Amino-4-*p*-aminophenylglyoxaline, and its salts (FARGHER and PYMAN), 239.

$C_9H_{12}O_3$  *cyclo*Pentane-1:1-diacetic anhydride (KON and THORPE), 700.

- $C_9H_{14}O_3$   $\beta$ -Methyl- $\beta$ -isopropylglutaric anhydride (KON and THORPE), 702.  
 $C_9H_{14}O_4$  *cyclo* Pentane-1:1-diacetic acid, and its silver salt (KON and THORPE), 700.  
 $C_9H_{14}O_7$  Trimethylsaccharolactone (HAWORTH and LEITCH), 816.  
 $C_9H_{16}O_4$   $\beta$ -Methyl- $\beta$ -isopropylglutaric acid (KON and THORPE), 702.

## 9 III

- $C_9H_7N_4Br$  2- and 4-*p*-Bromobenzeneazoglyoxalines (FARGHER and PYMAN), 243.  
 $C_9H_8NBr$   $\omega$ -Bromo-*m*-tolylacetoneitrile (GOUGH and THORPE), 1161.  
 $C_9H_9ON$   $\omega$ -Hydroxy-*m*-tolylacetoneitrile (GOUGH and THORPE), 1162.  
 $C_9H_9O_2Cl$   $\beta$ -Chlorohydratropic acid, preparation of (McKENZIE and WOOD), 835.  
 $C_9H_9O_4Br$  Methyl bromotsuginate (MANNING and NIERENSTEIN), 664.  
 $C_9H_9N_4Br$  2-5'-Bromo-2'-aminoanilino-glyoxaline (FARGHER and PYMAN), 246.  
 $C_9H_{10}ON_2$  Base, from reduction of 5-benzeneazo-4-methylglyoxaline (FARGHER and PYMAN), 253.  
 $C_9H_{13}O_2N$  Imide of *cyclopentane*-1:1-diacetic acid (KON and THORPE), 700.  
 $C_9H_{20}ON_2$  *as*-Dibutylcarbamide (WERNER), 1014.

## 9 IV

- $C_9H_{10}O_6NAS$  6-Oxalylamino-*m*-tolylarsinic acid (FARGHER), 989.  
 $C_9H_{10}O_7NAS$  5-Nitro-6-hydroxy-*m*-tolylarsinic acid (FARGHER), 990.  
 $C_9H_{10}O_3N_2AS$  2:7-Dimethyl-1:3-benzodiazole-5-arsinic acid (BAXTER and FARGHER), 1379.  
 $C_9H_{18}ONCl$  Dibutylcarbamy chloride (WERNER), 1013.

**C<sub>10</sub> Group.**

- $C_{10}H_8O_3$  Aldehyde, from hemlock tannin (MANNING and NIERENSTEIN), 668.  
 $C_{10}H_8O_4$  Acid, and its salts, from oxidation of aldehyde from hemlock tannin (MANNING and NIERENSTEIN), 668.  
 $C_{10}H_8S$   $\alpha$ -Naphthyl mercaptan, reaction of, with mercuric nitrite (RAY and GUHA), 1150.  
 $C_{10}H_9N$   $\beta$ -Naphthylamine, formation of diazamine-compounds from (NORMAN), 673.  
 $C_{10}H_{10}N_4$  Benzeneazo-4-methylglyoxalines (FARGHER and PYMAN), 249.  
 $C_{10}H_{12}O_3$  Ethyl *L*-mandelate, catalytic racemisation of (McKENZIE and WREN), 602.  
 $C_{10}H_{12}N_4$  2-Amino-5-*p*-aminophenyl-4-methylglyoxaline, and its salts (FARGHER and PYMAN), 250.  
 $C_{10}H_{13}N$  Neomethylhydrindamines, optically active, and their salts (HARRIS), 61.  
 $C_{10}H_{14}O_2$  Glycol *o*- and *m*-xylyl ethers (BOYD and THOMAS), 1243.  
 $C_{10}H_{14}N_2$  Nicotine, physical constants of (JEPHCOFF), 104.  
 $C_{10}H_{16}O_4$  2-Methyl*cyclopentane*-1:1-diacetic acid (KON and THORPE), 697.

## 10 III

- $C_{10}H_7O_5N$  4-Nitro- $\beta$ -naphthol (MORGAN and EVENS), 1132.  
 $C_{10}H_7O_5N_2$  2:4-Dinitro- $\alpha$ -naphthylamine, preparation of (MORGAN and EVENS), 1128.  
 $C_{10}H_9O_2N_2$  2-Phenylglyoxaline-4-carboxylic acid (FARGHER and PYMAN), 1018.  
 $C_{10}H_9ON_3$  2-Benzoylaminoglyoxaline (FARGHER and PYMAN), 248.  
 Glyoxaline-4-carboxyanilide (FARGHER and PYMAN), 228.

- $C_{10}H_9O_5Br$  Acetyl derivative of bromotsuginic acid (MANNING and NIERENSTEIN), 664.  
 $C_{10}H_9N_4Br$  4-p-Bromobenzeneazo-2-methylglyoxaline (FARGHER and PYMAN), 256.  
 $C_{10}H_{11}ON_3$  Base, from reduction of 5-benzeneazo-4-methylglyoxaline (FARGHER and PYMAN), 255.  
 $C_{10}H_{11}O_4Br$  Ethyl bromotsuginate (MANNING and NIERENSTEIN), 664.

10 IV

- $C_{10}H_9O_2N_2S_3$  Substance, from chloroacetic acid and the potassium salt of 2-thiol-5-thio-4-phenyl-4:5-dihydro-1:3:4-thiodiazole (RAY, GUHA, and DAS), 1312.  
 $C_{10}H_9N_2BrS_3$  Substance, from ethylene bromide and the potassium salt of 2-thiol-5-thio-4-phenyl-4:5-dihydro-1:3:4-thiodiazole (RAY, GUHA, and DAS), 1312.  
 $C_{10}H_{15}O_5N_2As$  3:4-Diacetylaminophenylarsinic acid (BAXTER and FARGHER), 1376.

$C_{11}$  Group.

- $C_{11}H_9N$  Indenyl-3-acetonitrile (INGOLD and THORPE), 152.  
 $C_{11}H_{10}O_4$  Ethyl ester of acid, from hemlock tannin (MANNING and NIERENSTEIN), 668.  
 $C_{11}H_{11}N$   $\beta$ -Naphthylmethylamine, preparation of (MORGAN and EVANS), 1140.  
 $C_{11}H_{19}O_4$   $\beta$ - $\omega$ -Carboxy-*m*-tolylpropionic acid, and its salts (GOUGH and THORPE), 1164.  
 $C_{11}H_{14}O_5$  5-*cyclo*Hexanespirodicyclopentan-3-one-1-carboxylic acid (INGOLD and THORPE), 364.  
 $C_{11}H_{14}O_5$  *cyclo*Pentane-1:1-dimalonic acid (KON and THORPE), 700.  
 $C_{11}H_{16}O_2$  Glycol mesityl ether (BOYD and THOMAS), 1243.  
 $C_{11}H_{16}O_3$  5-*cyclo*Hexanespirocyclopentan-3-one-1-carboxylic acid (INGOLD and THORPE), 372.  
 $C_{11}H_{18}O_3$  5-*cyclo*Hexanespirocyclopentan-3-ol-1-carboxylic acid (INGOLD and THORPE), 373.  
 $C_{11}H_{19}O_4$  2-Methylcyclohexane-1:1-diacetic acid, and its silver salt (KON and THORPE), 694.  
 $C_{11}H_{19}N_2$  Toluene-4-*N-n*-butyldiamines, and their hydrochlorides (REILLY and HICKINBOTTOM), 176.

11 III

- $C_{11}H_9O_3N$  4-Nitro- $\beta$ -naphthyl methyl ether (MORGAN and EVANS), 1133.  
 $C_{11}H_{10}ON_2$  1-Nitroso- $\beta$ -naphthylmethylamine (MORGAN and EVANS), 1141.  
 $C_{11}H_{11}ON_3$  2-Methylglyoxaline-4-carboxyanilide (FARGHER and PYMAN), 230.  
 $C_{11}H_{11}O_2N$   $\beta$ - $\omega$ -Cyano-*m*-tolylpropionic acid (GOUGH and THORPE), 1164.  
 $C_{11}H_{11}O_3N_3$   $\omega$ -Imide- $\alpha\alpha'$ -dicyanocyclopentane-1:1-diacetic acid (KON and THORPE), 701.  
 $C_{11}H_{11}O_2Cl$  Ethyl  $\alpha$ -chlorocinnamates (WALKER and JAMES), 1247.  
 $C_{11}H_{12}O_4N_2$   $\omega$ -Diimide of cyclopentane-1:1-dimalonic acid (KON and THORPE), 699.  
 $C_{11}H_{13}ON$   $\omega$ -Ethoxy-*m*-tolylacetonitrile (GOUGH and THORPE), 1163.  
 $C_{11}H_{13}O_2N_3$   $\omega$ -Imide of  $\alpha\alpha'$ -dicyano- $\beta$ -methyl- $\beta$ -isopropylglutaric acid (KON and THORPE), 702.  
 $C_{11}H_{14}O_2N_4$   $\omega$ -Diiminodiimide of cyclopentane-1:1-dimalonic acid (+  $\frac{1}{2}H_2O$ ) (KON and THORPE), 698.

- $C_{11}H_{15}O_4N_3$   $\omega$ -Imide of  $\alpha\alpha'$ -dicarbamylcyclopentane-1:1-diacetic acid (KON and THORPE), 701.  
 $C_1H_{17}O_7N$  Amide of cyclopentane-1:1-dimalonic acid (KON and THORPE), 699.

## 11 IV

- $C_{11}H_9O_7N_2S$  2-*p*-Sulphobenzeneazoglyoxaline-4:5-dicarboxylic acid (+  $2H_2O$ ), and its sodium salt (FARGHER and PYMAN), 258.

 $C_{12}$  Group.

- $C_{12}H_{10}$  Diphenyl, preparation of (KRIZEWSKY and TURNER), 559.

## 12 II

- $C_{12}H_{10}N_2$  Harman, preparation of, and its salts (PERKIN and ROBINSON), 971.  
 $C_{12}H_{11}N$   $\alpha$ -Indenyl-2- and -3-propionitriles (INGOLD and THORPE), 153.  
 $C_{12}H_{12}O_4$  5-cycloHexanespirodicyclopentan-3-one-1:2-dicarboxylic anhydride (INGOLD and THORPE), 363.  
 $C_{12}H_{14}O_5$  Anhydride of 3-cyclohexanespiro-1-methylcyclopropane-1:1':2-tricarboxylic acid (INGOLD and THORPE), 379.  
 5-cycloHexanespirodicyclopentan-3-one-1:2-dicarboxylic acid (INGOLD and THORPE), 362.  
*cis*-3-Hydroxy-4-cyclohexylcyclobutan-2-one-3:4-dicarboxylic anhydride (INGOLD and THORPE), 366.  
 $C_{12}H_{14}O_7$  Ethyl dihydrogen 5:5-dimethyldicyclopentan-3-one-1:2:4-tricarboxylate (INGOLD and THORPE), 383.  
 $C_{12}H_{16}O_4$  3-cycloHexanespiro-1-methylcyclopropane-1:1':2-tricarboxylic acid (INGOLD and THORPE), 379.  
*cis*- and *trans*-3-Hydroxy-4-cyclohexylcyclobutan-2-one-3:4-dicarboxylic acids, and their salts (INGOLD and THORPE), 364.  
 $C_{12}H_{13}O_5$  2:4-Dimethylcyclohexane 1:1-diacetic anhydride (KON and THORPE), 696.  
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